THE CHEMICAL COMPOSITION

of

TASMANITE SHALE OIL

With special reference to the

NITROGEN and SULPHUR

COMPOUNDS.

THE CHEMICAL COMPOSITION OF TASMANITE SHALE OIL.

Part I : GENERAL POSITION OF SHALE IN TASMANIA.

INTRODUCTION

Petroleum, both as a source of fuel and as a means of locomotion, has become one of the chief commodities vitally necessary to our civilisation. Australia is particularly unfavoured by nature, in that she is totally dependent upon outside sources for her supply of it, and, therefore, it is apparent that, living as we do in the fear of international strife, the need for research into this all-important element of our nation is very great. In a time of warfare, we would be wholly dependent upon the imported supply, which, in the year 1936-37 amounted to 282 million gallons of petroleum spirit valued at £4,525,939. It can be seen that the need for adequate internal resources of fuel is a very pressing question. As it appears that well-petroleum does not occur to any great extent in Australia, we should turn to the nearest substitute, i.e. the oil obtained during the distillation of oil-shale. The "Shale Bounty Act" was passed in 1917 in order to stimulate the production of this oil, and allows payment up to £67,500 per year based on a gallon production.

Shales occur in several regions in Australia, the chief of which are around the Newnes district in New South Wales and also in isolated patches in Queensland and Western Australia.

THE OCCURRENCE OF SHALE IN TASMANIA.

Of immediate interest to Tasmania are the deposits of oil-shale in the island, the largest, and most important, of which is situated in the north and north-western regions. It is an entirely different type of shale from that obtained from the other isolated deposits found in Tasmania, such as the Torbanitic shales of Prelenna. The estimated probable reserve in Tasmania is 27 million tons.

HISTORICAL INTRODUCTION.

The actual discovery of shale in Tasmania is not known, but the earliest publication dealing with the Tasmanian shales appeared in the "Papers and Proceedings of the Royal Society of Van Dieman's Land", for the year 1352. This was a paper contributed by J. Milligan and presented before the Society on the ninth of July, 1851. Another paper appeared in May of the following year.

on 9 July 1941

The next report of interest is that of Charles Gould. He submitted an article entitled "Resinous Shales (Dysodile) of Latrobe" to the Mines Department in 1861.

The most extensive work in the earlier period of the industry is that of R. M. Johnson (1), an eminent botanist, who, in 1888, published his"Systematic Account of the Geology of Tasmania."

Thus it can be seen that Tasmanite, as the shale at Latrobe is now called, has been known for nearly ninety years. However, it must be said that most reports dealt with the subject from the economic and investitive point of view, and not from that of scientific interest. If these investors had performed a systematic survey of the chemical composition of Tasmanite and the compounds occurring therein before entering into semi-commercial production, they would have been more in a position to follow and improve the various reactions occurring in the refining of the oil, and then their efforts might have been more fruitful.

In later years other publications have appeared on the Tasmanian shales, amongst which the following should be mentioned:-

(2) The Oil Shales of Tasmania.
A. McIntosh Reid.

(3) The Oil Shale Resources of Tasmania.
A. McIntosh Reid.

(4) The Tasmanite Shale Fields of the Mersey District.
W. H. Twelvetrees.

(5) The Oil Shales of Tasmania and New South Wales.
E. E. Kurth.

(6) On Tasmanite, a new Mineral of Organic Origin.
A. H. Church.

GEOLOGICAL INTRODUCTION.

(Condensed from the Tasmanian Geological Survey).

The Pre-Cambrian mica schist, consisting principally of quartz, biotite and muscovite of medium to coarse grain, and sericite quartz schists, are the oldest rocks in the district. Above these is the Cambrian formation consisting of quartz conglomerate, quartzite slate and fossiliferous sandstone. This formation lies below Ordovician Limestone and slate. Above these again are the pyroclastic slates and finally above these is the West Coast Range series of conglomerates and sandstones of the Silurian age. The Permo-Carboniferous system contains the beds of oil-shale and coal, which were laid down in regional synclinoria developed in the older rock formation.

The formation consists of basal conglomerate and sandstone, limestone, Upper and Lower Marine mudstone with intercalated coal measures, shales and grit. Folding is absent but faulting on a large scale is prevalent and there are large intrusions of dolerite associated with the faulting. As a result of these intrusions and faulting combined with the subsequent denudation of the overlying rocks, the Permo-Carboniferous rocks (and the Tasmanian shale seam) occur in a number of more or less separated blocks at different altitudes; the blocks being separated and bounded by diabase intrusions and faults respectively. The shale deposits are thus found in separate fields. The thickness of the seam varies from four to seven feet, and the seam consists of three distinct portions, viz. topshale, the middle band, and the bottom shale, the topshale being the thickest. The shale bed always consists of two main layers separated by a band of mudstone with a thickness from twelve inches to sixteen inches.

DEVELOPMENT OF THE INDUSTRY IN TASMANIA.

The first experimental plant was erected at Latrobe in 1901 by the Tasmanian Shale and Oil Syndicate of Adelaide, which was followed by that of another company in the next year. Between 1910 and 1930 no fewer than nine companies were formed to test the possibility of producing fuel oil from the deposits in this district (Latrobe) and surrounding districts. They had very little success, and in 1932 most of the existing companies amalgamated and since then have been more successful in the venture. The industry has not, however, progressed very much since the first plant. This is due, chiefly, to the lack of knowledge of the fundamental properties of both the shale and the oil obtained from it by distillation; this oil is unique in many properties when compared with other shale oils and a special technique is necessary in dealing with it.

THE NATURE OF TASMANITE.

Although Tasmanite shales were discovered as far back as 1851, the use of the word "Tasmanite" to designate the particular shales that occur in the north and north-western regions of Tasmania did not come into use until 1864, when it was first applied to this shale by Church (6).

Many opinions have been put forward concerning the origin of shales. Davis, writing on the origin of the Green River Shales, which occur in America, says:- "It is clear that the structureless material of Green River Shales probably originated in a collection of plant débris which has, by decomposition and the activities of bacteria and other microscopic organisms, passed into a jelly-like phase, which is to be found in certain kinds of peat deposits. The plant

remains which have been found characterising the shales of every locality from which they have been examined, are those of microscopic algae, mixed in a small percentage with pollen and similar parts of higher plants."

It is interesting to note, here, that D. K. Stewart records that the distillation of the spore cases of Lycopodium yield an oil similar to that of shale oil. Among other opinions put forward as to the formation of shale , we find that of Scheithauer, who writes:- "From the varying thickness of the bituminous shales, the bitumen content of which alone makes it profitable to work, it would appear that a large number of marine animals perished on certain occasions, probably as the result of volcanic outbreaks." Later Scheithauer quotes Potonie (Zur Frage nach den Urmaterialien der Petroleum) as showing that the Australian shales are "of a vegetative origin and owes its formation to the oleaginous algae, being a fucoidal coal and not a true shale." Cunningham-Craig (7) suggests that an oil-shale field can be looked upon as the grave of a former oil-field.

The Nature of the Tasmanite shale deposits is entirely different from that of the torbanitic deposits of New South Wales, although it is approximately the same age. There are present in the shale innumerable numbers of spore cases embedded in a matrix of clay, sand, pebbles of quartz, etc.

It appears that Tasmanite is definitely of a vegetative origin. The oil-producing substance as seen under the microscope consists of roundish discs which can just be discerned by the naked eye. Their average diameter as given by Singh (8) is 200-533 mu. The spores, when not damaged, are circular in shape, but, as Singh points out, it appears that during fossilisation, they have been distorted and ruptured.

The general consensus of opinion is that they are innumerable sporangia. This view is taken by Newton (9) and also by Johnson (1) who suggests that they are allied to the Lycopodiaceous macrospores, and they have been named by Newton 'Tasmanites punctatus'. Experiments performed by Stewart (10) and the present writer show that the distillation of Lycopodium powder mixed with three to four times its weight of Fullers earth, leads to the formation of a product somewhat similar to that produced from Tasmanite.

The shale itself is grey to brownish black in colour; it is definitely laminated in structure, as can be seen best in the weathered shales. The specific gravity varies from 1.72 to 2.62, while the spore case material has a density of 1.10. When a lighted match is applied to a piece of shale, it commences to burn giving off large quantities of carbonaceous smoke. The average yield is up to 38 gallons per ton, using the Crozier retort. The richness of the shale is in proportion

to the number of spore cases in it.

A typical analysis is -

Moisture	1.40%
Volatile matter ..	22.0%
Fixed carbon ..	6.4%
Sulphur	2.44%
Ash	70.2%

RETORTING OF THE SHALE.

The oil prepared from the shale does not exist as such, in the shale, but is formed during the pyro-bituminous decomposition of the oil-shale. Thiessen (11) during an investigation of American and Scottish shales writes "that the shales, as far as examined, do not contain oil as such, but that the oils derived from them are derived from organic matter contained in them. All identifiable matter consists of plant matter or plant degradation matter." The oil yielding material has been termed by Crum Brown 'Kerogen' and this word has come into general use to designate the oil-producing substance in oil-shales.

Kerogen has never been isolated, although many unsuccessful attempts have been made to extract this kerogen from the shale. Using solvent methods, Hentz (12), working on the Estonian shale 'Kukersite', succeeded in extracting about 75% of the bitumen, using hydrochloric and hydrofluoric acids, followed by chloroform extraction. Gavin and Adyelotte (13) also succeeded in extracting some 11% of solute using organic solvents. McKinney (14) published an article entitled "The Constitution of Kerogen". He extracted the shale with acetone followed by a chloroform treatment and a brown powder was finally obtained and its properties investigated. It must be kept in mind that kerogen is not a definite chemical compound. The production of shale oil probably takes place in two stages, as McKee says "When the oil shale is destructively distilled, it is doubtful whether any of the final products are liberated as such from the kerogen. The decomposition of oil from kerogen takes place in two stages. A primary decomposition occurs, in which the kerogen changes into a sulphuric acid-soluble solid, or semi-solid, bitumen. This intermediate product is not of the same composition as the kerogen, as indicated by its analysis and its ready solubility. This intermediate bitumen is unstable and a second decomposition changes it into the lighter oils of greater stability and higher 'saturation'".

With regard to the retorting of the Tasmanite shale oil, a most excellent account of the different factors effecting the yield during retorting and a detailed examination of

retorting in general has been given by Kurth (5) and a summary of his researches appears elsewhere (15). In order to avoid unnecessary repetition, reference may be made to the original thesis (5).

THE NATURE OF THE CRUDE OIL.

Kurth (15) writes - "The general character of Tasmanite shale oil is that it has a relatively high specific gravity and is an unsaturated asphaltic base oil and of moderate calorific value.

The crude oil has a very penetrating odour, which is principally a blend of Sulphuretted hydrogen, with more complex sulphides (such as allyl-propyl-sulphide) mercaptans, creosote and nitrogenous basic oil like pyridine. The nitrogen constituents are responsible for the clinging nature of the smell, while the hydrogen and other sulphides give most of the offensiveness."

Analysis of the crude oil gave the following results:-

C	79.34	H	10.41	O	4.93	N	0.31	S	4.93
							(McIntosh Reid - 3)		
C	81.9	H	10.7	O	4.6	N	0.27	S	2.5
							(Kurth - 5)		

The specific gravity varies between 0.931 and 0.956. Reid gives the calorific value as 22,625 and the flask point from 235°-260°. Neglecting the nitrogen, Church given the empirical formula $C_{40}H_{64}O_2S$ and suggests that it may be terpenic in origin. This latter statement concurs with the results of present research on the spore case concentrates performed in this laboratory. The spore case material has the approximate empirical formula $(C_{19}H_{29}O\quad)_7S_3N$, and is very resistent to chemical attack. It is acted upon by nitric acid of specific gravity 1.4 at an elevated temperature to give a nitration product with a moleculr weight of nearly 1000. Results tended to show that this product contained four carboxyl groups, one of which was alkylated. The nitration product has a probable terpenic structure.

Part 2 : DISTILLATION and HYDROCARBON ANALYSES.

INTRODUCTION.

It is readily acknowledged by petroleum technologists, that the supply of petroleum from oil-wells will not last forever; and among the naturally occurring petroleum substitutes is the oil obtained from the distillation and treatment of oil-shales. Quite a lot of work has been done on the oil-shales with regard to the method of retorting, the pyro-decomposition, etc., but not very much has been published on the constitution of the oil itself, especially on the different hydrocarbons that occur and the heterocyclic compounds contained in the oil.

Although the chemical constitution of petroleum has received much attention, there is a surprising lack of information resulting from the investigation of any one shale oil, with the exceptions of the excellent work published by Kogerman (16), Gustav Hellsing (17), Fukio Horie (18) and the various articles on the Scottish oil. However, as far as the present writer is aware, no systematic investigation has been made on the Tasmanite shale oil, and very little more on any Australian oil.

Research on shale oil presents a more difficult problem than the corresponding on well-petroleum and is a harder task than might be suspected at first. This is due to several factors, the chief of which are:-

(i) The relatively high percentage of nitrogen and sulphur makes the preparation of pure hydrocarbon mixtures very difficult, if not impossible. The work on the nitrogen constituents and the sulphur compounds was also very difficult, because there was the possibility of molecules occurring which contained both of these elements.

(ii) The high percentage of unsaturates, which leads to the formation of quantities of tarry masses when the oil is treated with sulphuric acid in a manner which is applicable to well-oils containing a much lesser quantity of this hydrocarbon type.

(iii) The occurrence of acidics and bases in such a quantity as to justify a separate and complete investigation on them.

(iv) The general inapplicability of the usual methods of chemical analysis, such as are published in the current journals on petroleum technology.

THE GENERAL CHARACTERISTICS OF THE OIL.

The oil, as supplied by the Secretary of Mines for Tasmania, was a mobile oil of black colour and very rank smell. The oil was not a crude oil in the true sense of the word (see note later) but was produced by a gentle and approximate isothermal distillation, the temperature never rising above 400°C. There is little or no hydrogen sulphide produced during this distillation, whereas in commercial retorting large quantities of hydrogen sulphide are found in the oil. Assuming that the production of the hydrogen sulphide is the result of the secondary decomposition mentioned earlier, the type of oil chosen for this research should, therefore, give more important information on the structure of the spore case material than similar work in the true crude oil, the crude being subjected to more rigorous temperature conditions and vapour phase cracking.

The oil had a specific gravity of 0.8540 @ 15° and a refractive index of 1.4684 at the same temperature. These values altered a little when the oil had been standing for some months, the specific gravity increasing to 0.8557, and the refractive index decreasing to 1.4672, the temperature again at 15°.

The above values of the specific gravity and of the refractive index, and also all proceeding ones in this paper, were obtained in the following manner:-

The Specific Gravity was measured by the Westphal balance corrected against pure distilled water, both before and after the series of observations had been made. If any small correction was thought necessary, the amount of that correction was derived from the data published by Beale (19). The correction to be applied to the refractive index measurements in the crude hydrocarbon analyses was based on the Eykmann equation and on the results of Kurtz and Ward (20), this corresponds approximately with

$$\Delta n_D = 0.60\, \Delta d_4$$

The Refractive Index (n_D) was found using an Abbé refractometer, the readings being standardised against a block of glass of known refractive index supplied with the instrument.

All percentages are volume-percent, unless specifically stated otherwise, and all temperatures are given in degress Centigrade, and are not corrected for the emergent stem. The results of the estimations are usually the average of two estimations, or in some cases, triplicates were thought necessary.

The percentages of nitrogen and sulphur in the oil were 0.342 and 2.22 respectively. The oil was examined for the presence of moisture, according to the method of Migray (21) and two determinations gave 0.24% and 0.26% of hydroscopic moisture. The absence of hydrogen sulphide was shown by two methods, viz. that

of Faragher, Morrel and Monroe (22) and also that of Wendt and Diggs (23). An examination for the presence of elementary sulphur using an inverted Halphen cotton-seed test (24) also gave negative results.

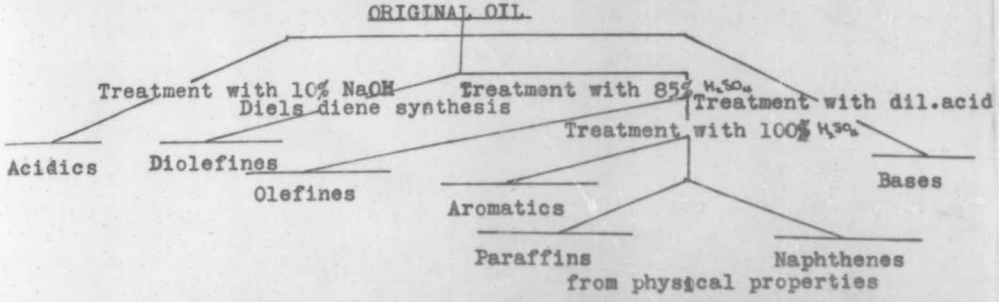
The results of the estimations of the different hydrocarbon types in the crude oil are shown below:- (NOTE: here, and in future, the word "crude oil" will designate the oil as supplied to the laboratory, the preparation of which has been described earlier.

	Percentage Removed	Sp. Gr. @ 20° of remaining oil	Refractive index ditto.
Original oil	nil	0.8447	1.4674
Dilute caustic wash	4.5	0.8415	1.4671
Dilute acid wash	3.2	0.8403	1.4667
Dehydration with sodium	0.0	0.8401	1.4668
Fuming sulphuric acid wash	56.1	0.7779	1.4387

Other estimations gave:-

Percentage of mercaptans 0.306
Percentage of di-olefines 5.7
Acetylenes present, but not determined.
Organic peroxides present, but not determined.

A rough plan of the analyses, in order of application, is given below. From the chart it can be seen that no allowance has been made for the presence of the thiophenic compounds. Other sulphur containing substances, such as mercaptans, were removed as far as possible, but the thiophenes and allied substances were counted in with the aromatics. Gurwitsch states that small amounts of such substances will not effect the estimations very much.



LABORATORY RESULTS

The shale oil, as supplied to this laboratory, was a light oil of nearly black colour with a chacteristic odour, density 0.8540 @ 15° and refractive index 1.4684. It contained 0.342% of nitrogen and 2.22% of sulphur.

The oil was fractionated by means of an iron drum of five gallons capacity, with an upright column at the top. This column was lagged with asbestos tape, and between two layers of asbestos was enclosed a spiral of nicrome wire, with increased spacing from the top downwards, up to a point 10 cms. from the top and to 23 cms. from the bottom. There were two windows at the top and bottom of the column in order to observe the flow inside the tube. The fractionating column had the following measurements:-

Total length of tube	103.5cms.
Diameter of tube	22.3mms. outside
	20.3mms. inside

and the drum:-

Height of drum	42.1cms.
Diameter of drum	27.3cms.

(see diagram opposite)

Inside the column, as a packing agent, was hung six yards of medium sized brass jack-chain in six lengths of one yard. At the top of the column was a drip gap with an exit tube leading down to a double surface condenser and receiving containers. The containers were equipped with internal worms, in which was a flow of cold water in order to completely cool the higher fractions. When fraction 'L' was reached the condensing system was replaced with a straight air condenser with a length of 163cms. and a diameter of 19.8mms. (see fig.1).

The heating system consisted of three ring burners. After the distillation had been running for 1.hr. 5' the current was switched on in the column, the current was 2.9amp. and this was gradually increased to 4.1amp. after 2hr. 50'. The last litre or so could not be distilled in the above apparatus, on account of the heat losses at the sides of the drum, and the residues were distilled in a one litre Pyrex distilling flask, the highest temperature reached was 353°. Distillation was not carried further than this on account of the cracking which took place. An examination of the chain after the distillation showed a slight black scale which peeled off easily, this discolouration was not apparent till fraction 'O' was reached as seen through the peep-windows.

Seventeen litres of the oil were placed in the drum and distilled at as near a constant rate as possible, with the following results:-

Table No.1.

Distillation Results.

Fraction No.	Thermometer Readings °C. Top min.	Top max.	Bottom min.	Bottom max.	Volume	Sp.Gr. @ 20°	Refractive Index @ 20°	Drum No.	dW/dT
A	36	60	15	90	60	0.6799	1.3857	15	1.69
B	60	70	98	106	414	0.6958	1.4038	13.4	28.85
C	70	80	106	113	162	0.7199	1.4046	13.3	11.68
D	80	90	113	116	227	0.7200	1.4060	13.2	16.67
E	90	100	116	124	125	0.7237	1.4097	13.1	9.38
F	100	110	124	130	256	0.7425	1.4130	13.1	19.00
G	110	120	130	135	261	0.7531	1.4205	12.9	19.64
H	120	130	135	141	497	0.7630	1.4242	12.8	37.9
I	130	140	141	149	544	0.7665	1.4284	12.7	41.65
J	140	150	149	156	529	0.7785	1.4329	12.6	41.2
K	150	155	156	163	956	0.7901	1.4411	12.5	75.6
	155	160	163	167		0.7968	1.4426	12.5	
L	160	165	167	171	841	0.8040	1.4446	12.4	75.65
	165	170	171	181		0.8095	1.4493	12.5	
M	170	180	181	192	910	0.8148	1.4523	12.5	75.0
N	180	200	192	213	2022	0.8298	1.4607	12.2	84.64
O	200	220	213	222	1920	0.8461	1.4657	12.5	83.6
P	220	240	222	242	1873	0.8713	1.4805	12.3	81.6
Q	240	260	242	273	822	0.8779	1.4848	11.5	36.1
R	260	280	273	294	864	0.8803	1.4932	11.5	38.0
S	280	300	294	315	778	0.8978	1.4992	11.4	34.9
T	300	320	---	---	843	0.9161	1.5077	11.4	38.2
U	320	340	---	---	705	0.9328	1.5183	11.3	32.8
V	340	---	---	---	175	0.9514	1.5227	11.3	--

The residue in the flask was hard black pitch. With regard to the colour of the fractions, A to C were colourless
D very pale yellow
E & F pale yellow
G to I yellow
from J. to N the colour gradually deepened from yellow to orange and from O to R from orange through port wine colour to deep red, while the last two fractions were nearly black, or rather a very dark brown.

From graph ii, it can be seen that there is a gradual increase in the mass of each fraction, until 200°C, and then there is a sudden decrease, but reaches an approximate constant mass towards the end of the distillation.

The above results were obtained on the freshly distilled oil, and, as this contained some moisture, it is to be expected that after the oil had been standing some time and the water particles had settled out, the values would alter, the density would become lower and the refractive index higher. The table below is based on the results when the fractions had been standing in corked bottles for a period of six months. During the intervening time, some of the fractions had been combined.

Table No.2.

Lot No.	Refractive index @ 20°	Drum No.	Specific gravity	Change in six months. Refr. Ind.	Sp.Gr.
A.B.C.	1.4042	13.4	0.7178		
D.E.	1.4097	13.4	0.7367		
F.G.	1.4200	13.0	0.7500		
H.	1.4269	12.8	0.7710	+0.0027	+0.0080
I.	1.4284	12.7	0.7761	0.0000	+0.0096
J.K.	1.4362	12.6	0.7948		
L.M.	1.4478	12.5	0.8178		
N.	1.4584	12.5	0.8380	-0.0023	+0.0082
O.	1.4638	12.6	0.8511	-0.0019	+0.0050
P.	1.4788	12.5	0.8773	-0.0017	+0.0060
Q.	1.4813	12.5	0.8799	-0.0035	+0.0020
R.	1.4880	12.4	0.8943	-0.0052	+0.0140
S.	1.4940	12.4	0.9040	-0.0052	+0.0062
T.U.V.	1.5094	12.2	0.9267		

SYSTEMATIC WASHING OF THE FRACTIONS TO DETERMINE THE ACIDIC AND BASIC CONTENT.

One hundred ml. of each fraction was taken and poured into a stoppered separating funnel and agitated strongly with an equal volume of 10% solution of sodium hydroxide for about ten minutes, allowed to stand till the two layers were completely separated, and the aqueous layer drawn off. The volume of the oil was

measured and the above treatment applied so long as the aqueous layer was coloured, or any diminution in volume of the oil took place. They were then washed with very dilute caustic followed by water, - Table No.3.

Secondly, the fractions were washed with 10% sulphuric acid in the same manner as in the caustic treatment, and the results were tabulated in Table No.4. A wash with dilute sodium carbonate solution followed in order to remove traces of acid, then the fractions were given a final wash with warm water. In Table No.7, the different fractions were treated in the same manner, using 25% acetic acid instead of the sulphuric. Parker states (26) that 25% acetic acid dissolves 1%-2% more basic substance, dissolves it more quickly, and causes less polymerisation.

Fraction	Table No.3. Percent of acidic material	Table No.4. Percent of basic material
A	0.0	0.5
B	0.0	0.5
C	0.0	1.0
D	0.0	1.1
E	0.0	1.0
F	0.0	1.1
G	0.0	1.1
H	0.1	1.4
I	0.3	1.6
J	0.4	2.0
K	0.5	2.4
L	1.5	2.5
M	2.0	2.5
N	3.0	2.7
O	3.5	3.5
P	3.5	4.0
Q	4.5	4.0
R	5.0	4.5
S	5.0	4.5
T	5.5	4.5
U	5.5	4.0
V	5.8	4.0

To indicate the progressive removal of the acidics and basics with the alkaline and acid washings, the following tables give the volumes of the residual oil after having been treated as above. The fractions were of an intermediate character and boiled between 150° and 240°.

Table No.5 the 10% sulphuric acid wash
Table No.6 the 10% caustic soda wash

Table No.5.

Fraction	First Washing	Second Washing	Third Washing	Fourth Washing	Percent Loss
K-2	97.2	97.1	97.1	----	2.4
L-1	97.0	96.8	96.8	96.0	2.5
M-7	95.8	95.6	95.6	95.5	2.5
N-11	95.0	94.5	94.3	94.3	2.7
O-8	94.5	93.5	93.0	93.0	3.5
P-10	93.7	93.0	92.5	92.5	4.0

Table No.6.

Fraction	First Washing	Second Washing	Third Washing	Fourth Washing	Percent Loss
K-2	99.8	99.5	99.5		0.5
L-1	99.0	98.6	98.5		1.5
M-7	98.5	98.0	98.0		2.0
N-11	98.0	97.0	97.0		3.0
O-8	97.0	96.5	96.5		3.5
P-10	96.5	96.5	96.5		3.5

Results on the oils which had been standing for six months:-

Table No.7.

Fraction	(a) Percent acidics	(b) Percent basics using 25% HA.
A.B.C.	0.0	3.8
D.E.	0.0	5.0
F.G.	0.0	1.4
H.	0.0	2.5
I.	0.0	3.5
J.K.	0.1	2.0
L.M.	2.1	2.4
N.	3.0	3.0
O.	3.8	3.5
P.	4.0	4.0
Q.	4.5	4.5
R.	5.3	5.0
S.	5.5	4.5
T.U.V.	5.5	4.5

Comparing Tables 4 and 7(b) - curves iv (2) and iv (3), it can be seen that the extractions with acetic acid gives a much greater loss than the corresponding sulphuric acid. This is probably due to the extraction of some other substance, or substances, which is not soluble in the dilute sulphuric, but

soluble in the acetic.

Dehydration of the Fractions.

After the oils had been freed of acidic, basic and some sulphur constituents as above, they were dehydrated as follows:- In Table 8, the fractions were dried over freshly fused calcium chloride, but in the following table, i.e. No.9, a more drastic treatment ensued. After the drying with calcium chloride, they were allowed to stand overnight in contact with metallic calcium, followed by the same procedure using metallic sodium. The fractions had the following characteristics -

Table No.8.

Fraction	Density @ 20°	Refractive Index.
A	0.6800	1.3858
B	0.6959	1.4039
C	0.7200	1.4048
D	0.7195	1.4063
E	0.7230	1.4098
F	0.7415	1.4130
G	0.7528	1.4200
H	0.7649	1.4254
I	0.7665	1.4286
J	0.7806	1.4330
K	0.7897	1.4380
L	0.8004	1.4419
M	0.8154	1.4494
N	0.8277	1.4567
O	0.8396	1.4612
P	0.8668	1.4758
Q	0.8763	1.4832
R	0.8764	1.4906
S	0.8958	1.4974
T	0.8999	1.5056
U	0.9311	1.5170
V	0.9500	1.5213

Table No.9.
(After the oils were 6 mths.old)

Fraction	Density @ 20°	Refractive Index	Drum No.
A.B.C.	0.7167	1.4065	13.5
D.E.	0.7366	1.4108	13.5
F.G.	0.7555	1.4213	13.0
H.	0.7708	1.4275	13.0
I.	0.7751	1.4305	13.0
J.K.	0.7858	1.4367	12.8
L.M.	0.8055	1.4475	12.8
N.	0.8281	1.4573	12.8
O.	0.8371	1.4618	12.7
P.	0.8542	1.4766	12.5
Q.	0.8683	1.4841	12.2
R.	0.8844	1.4913	12.0
S.	0.8939	1.4980	12.0
T.U.V.	0.9136	1.5079	11.8

From the above figures the following derived constants may be obtained, the Refractivity Intercept (35), the dispersion for the F-C interval, also the G'-C interval. This last one being necessary to conform with the results of Vlugter, Waterman and van Weston (94).

The interval G'-C can be calculated from the formula

$$n_{G'} - n_C = \frac{(1/\lambda_{\acute{a}} - 1/\lambda_c)}{1.9095}$$

(See Cauchy (95))

THE OLEFINE CONTENT.

The determination of correct olefine content is a matter of difficulty in such a case as this. Owing to the colour of fraction 'M' onwards, methods such as that of Mulliken and Wakeman (27) involving the use of bromine, could not be used, as even the lower fractions had sufficient yellow colour to mask completely the very similar colour of the bromine. Thomas, Bloch and Hoestra (28) suggest that bromine absorption does not give a correct value for the olefine content, especially when di-olefines are present, which is undoubtedly the case in the distillation fractions of the Tasmanite shale oil, (see later). The use of the Francis bromide-bromate method (29) was tried in the lower fractions, but it did not give concordant results, probably on account of the presence of cyclic olefines which, according to Cortese (30), give anomalous results. It is possible to use the bromination method in a manner such as the olefines are selectively attacked and not the aromatics. This is followed by distillation, but, however, it is impossible to separate the dibromides of the higher olefines from the unattacked hydrocarbons, in the case of the higher fractions.

Several methods were tried, including precipitating the unsaturates with metallic salts, and other methods, which formed heavy messy scums, or unbreakable emulsions. Therefore, it was finally decided to use the sulphuric acid treatment method. It is realised that this method has many disadvantages, such as the formation of polymers, incipient attack on other hydrocarbon types, etc. The action of sulphuric acid on such oils is very complicated, and much research has been spent on the problem, but no ideal strength has been found where one hydrocarbon type has been attacked, and the other left completely alone (see Brooks & Humphrey (31)).

Fisher & Eisner (32) have published an article on the effect of sulphuric acid of varying strength on petroleum oils, and they suggest that the point at which all the aromatics have been removed and there is incipient attack on the naphthenes and allied substances, may be found by graphing the variation in refractive index when the oil is washed with increasingly concentrated sulphuric acid. A similar series of observations were carried out with the Tasmanite shale oil, and the results are shown in Graph No.5.

It must be remembered that the constitution of the oil after the sulphuric acid treatment is not necessarily the same as before this operation, as polymerisation may take place, causing a rise of the specific gravity; there may be attack on substances with associated condensation which will give products in such a way that the result from the treatment of the oil with the acid has properties, both chemically and physically different from that of the oil minus the acid solubles, new paraffins and naphthenes being formed.

It is rather doubtful whether the term 'olefine content' should be used in preference to 'solubility in 85% sulphuric acid'. In such a complex mixture as this, a single compound may act as more than one hydrocarbon type. For example, it may be partly olefinic and partly naphthenic. There are many hydrocarbons containing a hexahydrobenzene nucleus with unsaturated side chains, and it is impossible to designate such a compound as either olefinic or naphthenic. It will act as either or both depending on its environments. As has been shown by Thomas, Block & Hoestra (28) an acid of 100% strength gives the best approximation for the volume-percent olefine content at room temperature, but in order to produce the correct figure for the refractive index, an acid of no less strength than 105% was required.

In order to obtain some idea of the action of different strengths of sulphuric acid on the oil, a representative middle fraction was taken and treated with gradually increasing concentrations of acid according to the method proposed by Fisher & Eisner (32). The refractive index of the untreated oil was 1.4812 and volume 100 ml.

Table No.11.

Acid Strength	Volume remaining	Refractive Index @ 15°
70	93.0	1.4778
75	88.0	1.4785
80	82.5	1.4796
82.5	80.5	1.4800
85	76.0	1.4820
88	60.5	1.4795
90	58.0	1.4765
96	51.0	1.4583
100	44.5	1.4364
105	39.5	1.4385

From the graph it can be seen that there is incipient attack on the aromatics when the acid strength reached about 85-87%, and that the complete removal of aromatics and the commencement of the attack on the paraffin-naphthene mixture starts from 100% to 105% sulphuric acid.

During both acid treatments the termination of the acid attack was considered finished when either the acid ceased to be discoloured, or when no heat was generated during the washings when the acid and oil were agitated together in a separating funnel.

The above authors (28) also make the assertion that the 98% acid method of Faragher, Morrell and Levine (79) and that of Ormandy and Craven (33) are not suitable on account of the the incomplete removal of the aromatics.

EXPERIMENTAL.

One hundred mls. of the oil was agitated with 85% sulphuric acid for ten minutes with cooling, the acid layer removed and the treatment continued as long as the acid was discoloured or heat generated. The corrected strength of the acid was 85.1% H_2SO_4.

Table No.12.

Fraction No.	Percent removed with 85% acid	On the residual oil Refractive index	Drum No.
A	40.0	1.4161	14.1
B	40.4	1.4159	14.1
C	46.0	1.4159	14.1
D	47.0	1.4158	14.1
E	46.0	1.4163	14.1
F	47.0	1.4177	14.1
G	45.0	1.4179	14.1
H	41.0	1.4280	14.1
I	45.0	1.4290	14.1
J	45.0	1.4297	14.0
K	44.0	1.4300	13.7
L	42.0	1.4344	13.6
M	40.5	1.4458	13.1
N	40.0	1.4515	13.1
O	40.0	1.4590	13.0
P	40.0	1.4690	12.4
Q	41.0	1.4788	11.8
R	40.0	1.4858	10.9
S	40.0	1.4930	10.8
T	41.0	1.4973	10.8
U	40.5	1.5027	10.8
V	40.0	1.5111	10.8

A second volume of the different fractions was treated with 100% sulphuric acid and the loss in volume measured when the acid was no longer discoloured. This loss gives a measure of the olefine plus aromatic content (28) and the residual oil treated with a further quantity of 105% acid and physical characteristics determined.

The residual oils were water white, had practically no odour, and did not decolourise weak potassium permanganate solution. They were washed with a dilute solution of sodium carbonate followed by a warm water wash. They were then dehydrated with calcium chloride, metallic calcium, and finally with metallic sodium. The refractive indices and densities were measured and derived values for the refractivity intercept and dispersion obtained. The resulting liquids were considered as mixtures of paraffins and naphthenes only, but it must be kept in mind that in such an oil as this, very complex molecules may occur, containing two or more rings per molecule and also in the higher fractions some of the side chains may be quite long. These side chains may contain double or triple bonds. Therefore, it can be seen that the attack by the sulphuric acid may be a more or less partial one, in which only part of the molecule is concerned, and from this there may be new molecules formed with different properties, consequently some methods of estimation may not agree with others.

Table No.13. (cp. No.9) Residual Oil after 85% Sulphuric Acid.

Fraction No.	Refractive Index	Drum No.	Density	n-d/2	Percent loss on Treatment
A.B.C.	1.4180	14.1	0.7184	1.0588	42
D.E.	1.4191	14.1	0.7212	1.0586	46.5
F.G.	1.4238	14.1	0.7462	1.0507	46
H.	1.4290	14.0	0.7616	1.0482	41
I.	1.4305	14.0	0.7645	1.0483	45
J.K.	1.4318	13.8	0.7751	1.0443	45
L.M.	1.4501	13.3	0.8079	1.0463	41
N.	1.4518	13.1	0.8286	1.0475	40
O.	1.4600	13.0	0.8442	1.0479	40
P.	1.4693	12.4	0.8481	1.0453	41
Q.	1.4795	11.8	0.8634	1.0478	41
R.	1.4868	10.9	0.8770	1.0483	40
S.	1.4940	10.8	0.8902	1.0489	40
T.U.V.	1.5055	10.8	0.8994	1.0458	41

Table No.14. Residual Oil after 105% acid

Fraction No.	Refractive Index	Drum No.	Density	n-d/2	$n_F-n_C/d \times 10^4$	% loss on treatment with 100% acid
A.B.C.	1.4111	14.5	0.7350	1.0436	95.2	58
D.E.	1.4115	14.5	0.7390	1.0420	95.8	54
F.G.	1.4157	14.4	0.7419	1.0447	96.7	49.3
H.	1.4178	14.3	0.7529	1.0414	98.0	46.6
I.	1.4205	14.1	0.7590	1.0410	100.0	47.1
J.K.	1.4171	14.2	0.7471	1.0453	100.0	55.8
L.M.	1.4394	14.2	0.8013	1.0395	97.6	62.6
N.	1.4257	14.3	0.7687	1.0414	98.7	61.6
O.	1.4184	14.2	0.7483	1.0443	99.8	62.0
P.	1.4293	14.2	0.7824	1.0383	98.3	60.6

Table No.14. (Cont'd.)

Fraction No.	Refractive Index	Drum No.	Density	n-d/2	$n_f - n_c/d$	% loss on Treatment with 100% acid
Q.	1.4425	14.1	0.7834	1.0424	101.8	59.4
R.	1.4444	14.1	0.8018	1.0435	100.2	61.0
S.	1.4503	14.1	0.8198	1.0404	112.1	63.8
T.U.V.	1.4625	14.0	0.8454	1.0399	100.3	66.6

From the foregoing tables the percentages of the different hydrocarbon types can be found. These are tabulated below:-

Table No.15.

Fraction No.	Olefines 85% acid solubles	Aromatics 100% acid solubles	Paraffins from optical date	Naphthenes
A.B.C.	42	16	21.8	20.2
D.E.	46.5	7.5	26.5	19.5
F.G.	46	3.3	16.6	34.1
H.	41	5.6	20.3	33.1
I.	45	2.1	17.5	35.4
J.K.	45	10.8	22.5	21.7
L.M.	41	21.6	5.0	31.4
N.	40	21.6	29.2	9.2
O.	40	22.0	--	--
P.	40	20.6	--	--
Q.	41	18.0	--	--
R.	40	21.0	--	--
S.	40	24.0	--	--
T.U.V.	41	25.0	--	--

The reason for the almost constant values in the latter part of the olefine estimations was as follows:- When the higher fractions were treated with 85% sulphuric acid, large quantities of sticky tarry masses were formed which, without centrifuging, completely inhibited the formation of the two layers, or by sticking to the sides of the vessel made it impossible to measure the residual volumes, and it was impossible to differentiate between ±1%.

The lack of values for paraffin - naphthene contents in the higher fractions is due to the impossibility of applying optical methods in fractions boiling above 200° (approx.) on account of their complexity. It can be seen that there are sudden fluctuations in the last two pairs of figures probably due to the break-down of this method.

THE PRESENCE OF DI-OLEFINES.

The presence of di-olefines was suspected on account of the yellow colour of the fractions and the slight gum formation in some of them. A certain fraction in which the presence of di-olefines was strongly indicated, was placed in a flask with 20% of its weight of maleic anhydride and heated in a water bath for three hours, at the end of which the oil was decanted off and the resulting cake of crystals filtered on a Buchner funnel to remove traces of adhering oil. The crystals were slightly brown and were soluble in alcohol, they were rectangular in shape and melted at 145°C.

To prove that ring formation actually had taken place 1.5 grm. of the maleic anhydride compound was gently heated with 2 g. resorcinol and 1 grm. of zinc chloride for several hours, the product being a dark intense red solid, which was soluble in alcohol and which turned yellow in alkaline solution. This was due to the formation of a phthalein, which could only arise from a closed system.

Different fractions were treated with maleic anhydride according to the method of Diels and Alder (34), and that of Kurtz and Heading-ton (35). One hundred mls. of the separate fractions were placed in 250 ml. conical flasks fitted with reflux condensers, and 20 grams of maleic anhydride added, the flasks were then heated on steam baths from one to three hours, at the end of which the oil was decanted off as much as possible, and the remaining cakes of crystals were filtered on fine filters in Buchner funnels to remove adhering traces of oil. Then the residual anhydride-compound was washed with dilute caustic soda and any oil remaining undissolved was added to the bulk of the oil, and the volume losses after this treatment were found.

After treatment, certain of the higher fractions had the following chacteristics:-

Table No.16.

Fraction No.	Percentage loss	Refractive Index now	Density
P.	8.5	1.4754	0.8647
Q.	9.0	1.4796	0.8751
R.	5.6	1.4877	0.8920
S.	8.0	1.4936	0.9006
T.U.V.	10.7	1.5062	0.9267

The presence of comparatively large amounts of di-olefines is interesting on account of the formation of gum in the different fractions, and the bright yellow colour in the lighter ones. According to Brooks (36) the presence of the yellow colour in cracked gasolines is due to the presence of hydrocarbons, containing conjugated double bonds, such as are found in conjugated

di-olefines and he gives several facts to support this hypothesis. The formation of resins is largely attributed to di-olefines also; Humphrey and Brooks (37) write: "Di-olefines are probably the cause of the resinification which has been observed when highly cracked gasolines are permitted to stand for several months." In some of the distillation products of the Tasmanite oil which had been standing for one year, the presence of gum was noticed in fractions, but another lot of highly fractionated oil from a previous investigator (5) which had been standing for six years showed presence and absence of gum thus:-

Table No.17.

Fraction °C.	Gum	Colour
-80	None	
80-85	None	
85-90	Very small amount	Light yellow
90-95	None	
95-100	Small amount	" "
100-105	None	
105-110	None	
110-115	None	
115-120	Small amount	Yellow
120-125	None	
125-130	Larger quantities	"
130-135	None	
135-140	Small amount	Orange

and from 140-195° gum appeared in all the fractions in greater or lesser quantities.

In the oil under present examination it was noticed in the lower boiling fractions that a dark yellow to brown oil sank to the bottom of the containing vessel, this gum being insoluble in the oil proper. The following notes were taken regarding the type of gum formed:-

A.B.C.D.E.	Rather dark orange, watery liquid
F.G.	A sticky, brown tar, the same in H & I but in smaller amounts.
J.K.	Orange-brown, watery liquid
L.M.	Light, amber tar
N.	Clear and 'O' nearly so, with just a few spots of gum as was also P.Q.R.S., but with increasing amounts of an amber coloured mobile gum
T.U.V.	Dark brown gummy mass.

These results were obtained on the fractions after they had been standing in corked bottles for a period of one year. The presence of the yellow colour in fractions is considered objectionable and it was found that, by refluxing the oil with Fuller's earth and redistilling, the colour was practically removed. Fifty mls. of the oil was placed in a flask and 5 grm. of Fullers earth added, then refluxed for two hours, at the end of this period the oil was nearly water-white and completely so when it had been

re-distilled. This was performed on fraction 'I' which was particularly badly discoloured. The Dubosc colorimeter reading against N/100 potassium dichromate was 2.18, while the reading of the same oil after it had been treated as above was 13, showing a nearly six-fold decrease in colour. This treated fraction on standing in an open test tube for three months showed no inclination to reform the yellow colouring matter.

Most of the fractions gave a positive reaction to the test of Young, Vogt and Nieuwland (38) for the detection of organic peroxides.

THE TERPENIC-LIKE OLEFINES PRESENT.

The presence of terpenic-like hydrocarbons in oils has been a subject of debate for some time, especially on the Burmah and Borneo petroleum crudes. Carpenter, working on Burmah petroleum) on the fractions boiling between the limits 150-180°, i.e. the limits within which the terpenes are likely to be present, found on extracting it with aniline at a low temperature that terpenes were present in a small quantity. Crudes from Borneo and Java are reported to have a terpenic odour, and, in some cases, they form a skin on being exposed to the action of atmospheric oxygen, as in the case of the drying oils.

From the smell of the oils during some of the operations, and from certain other indications, it was suspected that terpenic-like materials might be present in the shale oil. The oil was subjected to the action of moist hydrogen chloride gas for a period of five hours, which resulted in the formation of thick black tar that stuck to the sides of the containing vessel. After trying unsuccessfully to extract the dihydrochlorides thus formed, it was decided to abandon this method.

DOUBLE SALTS WITH MERCURIC ACETATE (39 & 40)

500 ml. of the oil was mixed with 35 ml. of methyl alcohol containing 7 gms. of mercuric acetate in solution; this was shaken for a period of 18 minutes and then water and potassium iodide added and the mixture shaken for a similar period. The water-methanol layer was then drawn off. Hydrogen sulphide was passed through the aqueous layer as long as any mercuric sulphide was precipitated; the liquid was filtered and the filtrate steam distilled and the light yellow distillate collected.

Refractive index of first drop	1.4481
Refractive index of last drop	1.4840

This liquid was re-distilled under reduced pressure and the fraction corresponding to boiling point limits of 150-180° at atmospheric pressure set aside for examination. This fraction had an index of 1.4390, while that of the residues was 1.4660. If terpenes were present at all, on dehydrogenation p-cymene should be formed. The fraction was heated with half its weight of sulphur according to the procedure of Ruzicka (41) at 200 ± 5° for twenty-two hours and redistilled, the liquid coming over at 175-180 was put aside. This was a bad smelling oil of index 1.4386 at 21° after treatment with sulphur, while before treatment it was 1.4390. This product was shaken with sodium plumbite followed with a dilute solution of potassium permanganate and extracted with benzene, again distilled and a cut taken between the temperature limits of 175-177°. However, the properties of this fraction did in no way correspond with that of p-cymene.

HALOGENATION.

The lack of successful results using the above method was probably due to the combination of the sulphur with the olefinic terpenes (C.A. 27/3927) so some of the oil boiling between 150-180 from the mercuric acetate treatment, was dissolved in about 6 times its volume of carbon tetrachloride and cooled to -14° with ice and salt. When the whole of the mass of the oil had reached the temperature of -14° about an equal volume of bromine in carbon tetrachloride added, this bromination seemed to proceed evenly enough, the bromine was added slowly drop by drop from a burette with constant stirring and the product allowed to stand at -10 for some time. On pouring off the super-natant liquor a small crop of yellow crystals was found on the bottom of the beaker; about 1 ml. of alcohol was added. The major portion of the crystals dissolved and when the alcohol had evaporated, there remained a small crop of feathery white crystals which appeared to melt at 173° but incipient charring took place at this temperature. The supposed terpene tetrabromides were distilled with 2% of iodine (42) under reflux until hydrogen bromide had ceased to be given off. After the carbon tetrachloride had been removed by evaporation, the liquid was distilled, and a constant boiling fraction was collected. This boiled at 169° and further distillation produced a dark liquid smelling faintly of terpenes with a boiling point of 168 & 170° and a refractive index of 1.4966.

The above results were taken as an indication that terpenic hydrocarbons might be present in this oil. A larger volume was taken for examination thus:-

250 mls.	of cut	J	boiling-point		140-150
350 mls.	"	" K	"	"	150-160
350 "	"	" L	"	"	160-170
350 "	"	" M	"	"	170-180
300 "	"	" N	"	"	180-200
1600 mls.					

This oil was treated with the appropriate amount of mercuric acetate with methyl alcohol as before, agitated mechanically and the terpenes liberated with sulphuretted hydrogen. The residual oil, after it had been treated with mercuric acetate, was lighter in colour and had a much less offensive smell. The volume of the oil remaining was 1072 ml. so that the percentage loss on mercuric acetate treatment was 33%. The oil was again treated with mercuric acetate as before and the volume was then 950 ml.

The refractive indices and densities of the extracted olefines were:-

	First Washing	Second Washing
Refractive Index at 20°	1.4455	1.4476
Density at 21°	0.7866	0.7864

The liberated unsaturates were washed with water and extracted with ether, and the etherial layer washed with warm water and distilled. The first cut being water white and possessing the smell of sulphur compounds, and the second cut was pale yellow with the same garlic-mercaptan-allyl smell as had most of the proceeding ones.

In the distillation, the temperature seemed to go up in distinct steps. The results of this distillation are shown below.

Table No.18.

Cut	Boiling Range	Constant value in Range	Refractive Index @ 20°	Drum No.
1	95-105	---	1.3800	12.6
2	105-145	---	1.4330	12.6
3	145-155	---	1.4380	12.5
4	155-160	157	1.4408	12.5
5	160-165	162	1.4436	12.4
6	165-170	169	1.4454	12.4
7	170-175	---	1.4491	12.4
8	175-180	---	1.4501	12.5
	Residues		1.4656	

Table No.18 Cont'd.

Cut No.	Density @ 20°	$n_D - n_C/d \times 10^4$	Refractivity Intercept
2	0.7587	126	1.0437
3	0.7621	126	1.0570
4	0.7719	126	1.0549
5	0.7796	125	1.0546
6	0.7942	124.7	1.0483

All the fractions decolourised potassium permanganate solution readily and absorbed bromine energetically. An aliquot part was brominated and the Hydrogen bromide removed with alkali; the resulting liquid was distilled and the fraction coming over at about 175° was collected separately and its characteristics found.

Refractive Index @ 20°	1.4497
Density @ 19°	0.8013

Nitration was attempted, but no nitro-compounds could be found. The unsaturates were dehydrogenated with sulphur and selenium and the same procedure carried out, but no p-cymene could be isolated, although a distinct odour of terpenes was present. This smell was distinctly terpenic and rather like aniseed or oil of wintergreen. It gave no colour with ferric chloride.

From the above results, it can be seen that no direct evidence is forthcoming to prove that terpenes are present in the Tasmanite

THE NITROGEN CONSTITUENTS

Part 111. INTRODUCTION.

Nitrogen is present in all shale oils; the percentage in Scottish shale varies from 0.6% - 1.3%, while in Estonian oils the content is 0.25% (16). In Colorado it varies from 1.501% - 1.855% according to Franks (43). Tasmanite oil has a nitrogen content of 0.27% (5).

As regards the characteristics of the bases from Estonian shale oils, P. N. Kogerman (44) gives the following results:- "The pure bases separated from the shale oil formed a reddish liquid, with a quinoline-like odour sp. gr. 0.9731 @ 15 and n=1.539/19°." The nitrogen content of bases was 8.59% and they belong to the derivatives of the pyridine and quinoline series. The methyl and dimethyl derivatives of pyridine have been isolated from shale oil by Ihlder (45) but as far as can be ascertained, these lower homologues of this series do not occur in Tasmanite shale oil.

The type of nitrogen compounds produced during the distillation of shale oil depends on several factors, the chief of which are:- the time and rate of heating, the retorting method and the type of distillation, presence or relative absence of air or water. The main products are members of the pyridine or quinoline series, but heterocylic compounds of pyrrole nature seem to occur. Petrie (46) reports that a brown pyrrol-red precipitate was formed when the oil obtained from the torbanite of N.S.W. was allowed to stand. This oil gave the isatin test characteristic of pyrrol compounds. Accounts of an oil from Colorado giving the same deposit and also the "pyrrole reaction" are recorded by McKee. As will be seen later, some of the higher fractions of the Tasmanite shale oil gave exactly similar results,both with regards to the precipitate and also to the colour developed when a pine splinter moistened with hydrochloric acid was held in its vapours.

Up to the present, the heterocyclic nitrogen compounds in shale oil have not had much careful study, but in Japan under Fukio Horie, and in America and Estonia these researches have received a new impetus.

The first work published on the nitrogen compounds of shale oil was that of Williams (47) on Dorsetshire shale, in which he remarks on their bad smell; this seems to be an ever recurring observation on the shale bases. He reports that they burnt with a brilliant smoky flame, and that they were soluble in alcohol and ether and gave a precipitate with copper nitrate - characteristic of picoline salts. He isolated pyridine and some of its homologues namely methyl and dimethyl pyridine and parvoline, and also noted that some of the vapours had a pyrrolic nature.

Robinson (48) recorded the presence of nitrogen compounds in Scottish shale oils, and proved that the substances were members of the iso-quinoline series and not of the quinoline series. He named them leucoline, iridoline, cryptidine, tetracoline, pentacoline, hexacoline and octacoline. These bases occurred in the fraction boiling between 270° and 390° and had the series formula $C_nH_{2n-11}N$, corresponding to the quinoline members. In reference to the formation of salts, he writes:- "Attempts were made to get crystalline salts from the mixed bases, the double chlorides of Pt, Au, Cd, Hg, Pb, Zn, were tried but without success, only resinous sticky masses being obtained. The same failure in getting crystalline salts was experienced when the bases were treated with sulphuric, hydrochloric, nitric and oxalic acids". This failure is very interesting in the light of the results of the present writer, who obtained the same results, working on corresponding substances, but managed to find one of the reasons for the formation of these tarry masses.

Garret and Smythe (49) also working on Scottish shale oil, but on a lighter fraction, succeeded in identifying seven members of the pyridine series, namely, pyridine, picoline, lutidines, and collidines. These were identified by conversion to the corresponding acids with potassium permanganate. They also prepared some of the aurichlorides of the bases.

Morrel and Egloff (50) have reported the presence of pyridine derivatives similar to those of Williams, in Green River shale oils.

Beilby (51) has published some results on the nature of the bases in the Scottish oils, but no compounds were actually identified.

Franks (43) has written an article on the Colorado shale oils, in which he discusses the sulphur and nitrogen compounds in this oil, and the change from unsaturates to saturates during destructive distillation. He does not attempt to isolate any one compound but writes in his summary:- "Colorado shale oils and their fractions contain much nitrogen, which seems to be present as basic compounds, and complex, unstable, unsaturated substances of high molecular weight ...." and later "The simultaneous loss of nitrogen and sulphur and the increase in saturation by cracking suggest the hypothesis that the saturated oils thus formed are produced from unsaturated substances containing sulphur and nitrogen which are easily decomposed under the conditions that obtain during a destructive distillation."

Similar researches are in progress at the present time, the most noteworthy are those of Kogerman in Estonia and of Eguchi in Japan.

Kogerman (44) gives a detailed account of the method used to obtain the purified bases. He also records the fact that some of the higher fractions failed to give crystalline salts (cp. Robinson's remarks above). Kogerman succeeded in identifying pyridine, but although he remarks that the higher boiling ones belong to the pyridine and quinoline series, no direct evidence is shown beyond the smell, that this is so. Three tables are given showing the results of the fractionation of the bases, some of which are published later.

Eguchi (52) has reported the presence of members of the pyridine series in Fushun shale oil and has confirmed the following:-

2 - methyl - pyridine
2,6 - dimethyl - pyridine
2,4 - dimethyl - pyridine
2,6 - methyl - ethyl - pyridine
2,4,6 - trimethyl - pyridine.

A glance through the above summary of articles on the nitrogen-containing compounds in shale oil from different parts of the world would indicate that they are chiefly members or derivatives of the pyridine and quinoline series. However, compounds of a pyrrolic nature also occur. They have an offensive odour and darken on exposure to light and to the atmosphere. In most cases crystallisable compounds are not formed with metallic salts but only sticky resinous masses result. The results of the present research are fairly typical, except in the absence of the lower members of the pyridine series.

THE BASIC CONSTITUENTS OF TASMANITE SHALE OIL.

EXPERIMENTAL.

As it can be seen from foregoing results, the amount of material removed by acid washing varied from nil to nearly six per cent. One litre of the crude oil was treated with an equal volume of dilute sulphuric acid (the exact strength of the acid being 14.6 per cent) and agitated mechanically for several hours, allowed to stand overnight, and the sulphuric acid layer removed. The oil was again treated with acid (½ vol.) and the acid layer removed; the operation was repeated with 250 ml. of acid and the three acid washings united. The dirty coloured acid washings were rendered alkaline with caustic soda and the liberated bases were extracted with ether, the ether removed and the residue steam-distilled and again extracted with ether. The oil remaining after the removal of basic material contained only 0.186% of nitrogen.

The separated bases, in the first instance, i.e. together with hydroxides of iron and aluminium, were a light brown scum, smelling very strongly - the odour being reminiscent of pyridine, quinoline and a garlic smell, with a faint trace of a peppermint-like odour.

The aqueous residues were united, the liquid was very slightly yellow in colour and had an odour like stale beef-tea. It was extracted with benzene and chloroform to remove traces of bases, but with no success. Density and refractive index measurements were applied to the organic solvents as a criterion for the presence of bases. There was only a difference of 0.0023% in the refractive index and 0.0007% in the density of the benzene after having been treated with the aqueous liquor. However, when the residues were steam distilled about 0.5 ml. of an oil was obtained, which was added to the separated bases.

The mass of the bases was 28.4 grm. corresponding to 3.32% of the solution. They were again converted to sulphates and treated with ether to remove traces of hydrocarbons, neutralised and again extracted with ether. The purified bases were light yellow in colour, smelling of quinoline, with a green fluorescence. They contained 8.26% of nitrogen and 0.37% of sulphur. The density at 20° was .9804[8] and the refractive index at the same temperature was 1.5885. The bases were fractionated in a small flask with a 12 bulb fractionating column attached with a straight tube single surface condenser (length of tube 180 mm. and bore 6.0 mm.). The first drop occurred at 98°, the temperature remained constant for a short period at 99°, and 105°, but then immediately ascended to 210°, with short steadyings at 217° and 231°. The b.p. had a definite constant value at 239.

Table No.20.

Lot.1. Fraction No.	Temp. Limits.	n^{15}_{D}	% Vol.	Drum No.
A-1	10-100	1.4973	17.3	9.0
B	100-101	1.5116	8.6	8.5
C	101-105	1.5128	4.0	8.5
D	105-231	1.5121	1.7	8.3
E	231-240	1.5180	22.6	8.0
F	240-250	1.5274	17.3	7.2
G	250-270	1.5310	21.9	6.8
H	270-290	1.5428	1.3	5.3

The first fractions were colourless but developed a light yellow colour on standing (cp. Delaby & Hiron (53)), while the higher fractions varied progressively from light yellow through amber colour to deep brown. All fractions deepened in colour on standing. It is interesting to note here, that Delaby and Hiron (see above reference) writing on the alkyl quinolines, say:- "The alkyl quinolines are liquids of strong odour, light yellow colour, the colour gets deeper according to the increasing molecular weight. Ethyl quinoline is nearly colourless when freshly distilled and under the same conditions butyl quinoline is straw-yellow, finally it takes a brown-red colour, which deepens according to the time of preservation." (53) 'sur les alcoyl-Py-quinoleines'.

GENERAL REACTIONS OF BASES.

The bases gave the following reactions:-

(i) no carbylamine reaction

(ii) no brisk evolution of nitrogen with nitrous acid, when an aqueous suspension was mixed with an equal volume of chilled acetic acid, showing the absence of primary amines.

(iii) no crystalline derivatives were formed with methyl iodine, but after standing in a sealed tube for a period of six months, a thick, more or less solid, tarry substance was formed, dark red in colour.

(iv) Diazotisation.

Four drops of the bases were added to 2 ml. of water containing four drops of sulphuric acid, cooled to 3° then 2 ml. of a 10% solution of sodium nitrite was added with gentle agitation, chilled to 0° and a further 2 ml. of 3% nitrite added, followed by the addition of 0.2 grm. of beta-Napthol dissolved in 2ml. of 10% NaOH. The resulting solution was a brilliant green with a strong fluoresence, followed by an immediate precipitate of a dark green powder. The solution was then treated with dilute soda carbonate solution, which had the effect of differentiating the precipitate into two parts.

At this point, it is interesting to compare the results of Kogerman (16) who, working on similar bases from Estonian shale oil, obtained the following results. (Kogerman fractionated the Estonian bases into 5° cuts and to make the comparison lucid, average values were calculated for 10° intervals, except in the first two sets of figures.)

Temperature Limits	Refractive Index 16°	Specific Gravity 10°	Colour and Odour
90-160	1.481	--	Colourless;
160-220	1.501	--	pyridine-like odour
220-230	1.520	0.9553	Yellow;
230-240	1.532	0.9722	Quinoline-like
240-250	1.547	0.9560	odour.

It seems probable from these figures that, in the Estonian oil, true tertiary amines predominate, whereas in the Tasmanite oil other types of nitrogen-containing bodies are present. These latter non-quinolinic substances possess low refractive indices and low specific gravities, and assuming, apart from this, that similar compounds occur, this assumption would explain the greater increase in the properties tabulated above compared with Table 21.

DETAILED EXAMINATION OF BASES.

A larger volume of the oil was taken and an equal volume of 13% sulphuric acid was added and agitated with mechanical stirrer with baffle plates for a period of fourteen hours, and the purification treatment carried out as before. This time, the bases had the following characteristics:-

Refractive index	1.5260 @ 15°
	1.5225 @ 25°
Specific gravity	0.9717 @ 20°
Percentage of nitrogen	8.41
Percentage of Sulphur	0.27

In odour they were characteristic of the shale oil nitrogenous bases, i.e. a mixture of pyridine and quinoline with a faintly lingering peppermint smell, which became more pronounced when the bases were tasted. The smell of the bases lingered on the hands even after frequent washings, and the physiological action was most pronounced, the vapour producing most acute head-aches across the eyes and at the nape of the neck, together with a general sick feeling.

The purified bases were distilled several times in a 100 ml. pyrex flask with fractionating column and condenser of special design, which was completely made from Pyrex glass as the hot bases attacked rubber energetically. The column was made from 15 mm. Pyrex tubing fused at both ends to an inner one of 6 mm.

Table No.21.

Lot II.

Fraction No.	Temperature Limits	Refractive Index	Volume %	Drum No.	Constant temp. in range.
A-4	15-101	1.4975	9.6	9.1	--
B-5	213-220	1.5080	8.2	8.2	--
C-6	220-230	1.5096	10.4	7.9	227.5
D-7	230-240	1.5135	13.0	7.6	234.4 & 237
E-8	240-250	1.5190	11.3	7.4	244.6
F-9	250-260	1.5262	11.6	7.0	257
G-10	260-270	1.5270	12.6	6.8	264
H-11	270-280	1.5305	17.1	6.1	277
I-12	280-290	1.5390	8.2	5.9	--

diameter; the encircling jacket of air between the two tubes was evacuated with a Cenco Hyvac pump. The inner surface of the outer tube, and the outer surface of the inner tube having been silvered previously in order to reduce radiation losses. This was accomplished by the reduction of silver nitrate with formaldehyde. Inside the inner tube was fixed a helix of aluminium wire having about three turns per cm. In order to reduce contamination to a minimum, the flask was fused on to the column, and the column fused to the downward exit tube with the condenser attached.

DISTILLATION RESULTS.

An amount of liquid distilled before 100° with a slight constant value of R.F. at 87°, the thermometer thread then rose to 166° in three seconds and from 165° to 190° in seven minutes, remained constant at 197°, rose again to 236° and then to 260° and finally to 273°, from 273° onwards there was no discontinuenty in the temperature.

Cabin No.33.
Lot.111.

Fraction No.	Boiling Range	Volume	Constant value of R.F.	Density
X-6	15-80	4.0	--	0.8107
G-5	80-100	5.7	87	0.9993
Y-3	166-213	3.0	197	0.9270
D-8	213-238	15.9	236	0.9513
R-9	238-250	11.1	245	0.9778
C-8	250-270	6.1	260	0.9803
A-4	270-290	7.0	273	0.9891

Fraction No.	Volume Percent	Refractive Index @ 20°	Average Mol. Wt.	Nitrogen Content%
X	7.6	1.3712	---	---
G	10.8	1.4795	---	---
Y	5.3	1.5070	128.3x	10.89
D	30.1	1.5128	158.1x	10.01
R	21.0	1.5199	169.9	9.39
C	11.5	1.5200	174.9	9.10
A	13.9	1.5349	171.8	8.89

except in the cases marked 'x' the molecular weight was determined by the depression of the freezing point, using cyclohexane as the solvent (cryoscopic constant of cyclohexane = 20000 Muscarelli & Benati (64)). In the cases marked 'x' the molecular weight was found by the Victor Meyer method which, according to many authorities is inclined to give slightly low values, on the other hand the former method is supposed to give slightly high values.

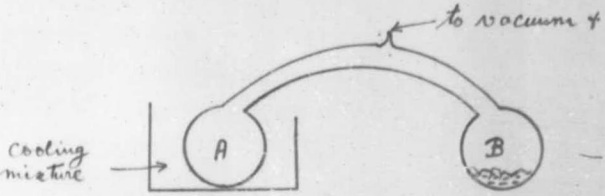
If there was any marked alteration from normal atmospheric pressure, the temperature of the boiling point was corrected according to the following equation

$$T = \frac{(273.1 + t)(2.8808 - \log p)}{\phi + .15\ (2.8808 - \log p\ )} \quad \ldots\ (66)$$

The first two cuts X and G were united and distilled under more controlled conditions, the first drop occurring at 35° and smelling strongly of ether plus a little basic smell; the temperature then rose to 98.7-99.0 and finally to 100°. Refractive index measurements of these cuts gave the following results:-

Fraction No.	Boiling Range	Volume	Refractive Index
X+G-i	35-36	2.1	1.3684
X+G-ii	98.7-99.0	1.7	1.4873
X+G-iii	100	5.6	1.3455

It is supposed from the above that there was some base soluble in water and which probably formed azeotropic mixture with it. This base was converted into its sulphate and washed with ether, then the water was removed and the etherial solution dehydrated. The aqueous solution was neutralised and the freed base extracted with ether, the ether removed and the supposed base distilled in a flask of the following construction -



The bulb 'B' contained the base, together with a lump of freshly ignited calcium oxide, and the small amount of liquid that came over into bulb 'A' was removed and centrifuged. There was less than 0.5 ml. of oil but it had a refractive index of 1.4961 and a boiling point of 179.2-179.5; it was nearly colourless with a slight green fluorescence.

Summary of Basic Liquor boiling in the Fraction below 100°C.

The only substance isolated was a small quantity of liquid with a boiling point of 179.2-179.5 and a refractive index of 1.4961 @ 10°. No picrate could be produced and the base was slightly soluble in water as shown by refractive index measurements. The only substance that has properties near that of the

above is 2,4-methyl-ethyl-pyridine (see C.A. 23/391.) which has been isolated from Fushun shale oil by Kouchi. The properties of this alkylated pyridine are given as:-

B.P. at 768 mm.	179-180
Refractive Index @ 25	1.4953

One might suggest that the compound isolated from Tasmanite might be 2,4,methyl-ethyl-pyridine, but this is, however, only based on the above facts.

There was also a trace of another substance boiling at about 99° with a refractive index of 1.4824. The value of the refractive index makes the occurrence of aliphatic amines, such as iso-amyl amine, impossible and at present no explanation can be offered as to explain the nature of this substance.

FRACTION Y - 3.

Boiling range	165-213° with constant value at 197°c.
Density	0.9270
Refractive Index	1.5070
Nitrogen content	10.89%
Molecular weight	128.3
Volume percent	5.3%

When this fraction was distilled, the apparatus for distillation having been described earlier, the first drop occurred at 173°. After this primary distillation, the different fractions were distilled again in a small flask of about ten ml. capacity, equipped with internal heating in the form of a small helix of platinium wire which was heated from a small 50 watt transformer at 24 volts. The distillation temperatures were measured, using small Anschutz thermometers graduated in 0.2 degrees; the criterion for the acceptance of one substance being that all of the distillate must come over within ±0.5°. One must realize that, in a problem such as this, it is impossible to completely separate the individual components by exhaustive distillation. However, the above criterion was taken as close enough for the present research on account of the other experimental errors. (c.p. Ganguli and Guha (56)).

Fraction No.	Temperature limits	Refractive Index	Constant value of t.	Vol.% on whole	Picrate m.p.
Y-3/(i)	173-175	1.4984	174	1.7	122° & 154°
Y-3/(ii)	198-199	1.5004	198	1.8	n.o.
Y-3/(iii)	205-207	1.5054	207	1.4	n.o.

n.o. = not obtainable.

Further fractionation and purification gave the following constants for the different cuts -

Fraction Y-3/(i).

Corrected boiling point	173.2°
Refractive Index	1.4984 @ 20° 1.4966 @ 25°
m.p. picrate	122°? and also @ 154°
Density	0.9181 @ 18°

The picrates were prepared in the following manner:- To one ml. of the base was added 5.ml. of 50% acetic acid in which was dissolved 2 grm. of picric acid, the base being dissolved in 35 ml. of 50% acetic acid - (57). When the crystals had been deposited they were centrifuged from the mother liquid and recrystallised from alcohol, washed and dried and the melting point found by the usual laboratory method. In this fraction the picrate melted at 154 degrees, but there were a few crystals which seemed to melt at 122°. This was, however, uncertain.

Now fraction Y-3/(i) in the light of the refractive index, density, molecular weight and nitrogen content, agreed very closely with such pyridine derivate as γ-collidine, the corresponding data for 2,4,6,trimethylpyridine are:-

Boiling point	172.6°
Density	0.917
Refractive Index	1.4980
Nitrogen Content	11.6
Molecular Weight	121.1
m.p. picrate	155-156

These figures agree very closely with the calculated ones for γ-collidine, and from this agreement it is assumed that the chief compounds found in the fraction boiling about 200° are tri-alkyl pyridines.

Analysis of the available data showed -

	b_p	n_d	m.p.picrate	density
5,ethyl-2,methyl-pyridine	174			
2,4,6,-trimethyl-pyridine	172	1.4959^{25}	156	0.917
2,3,6,-trimethyl-pyridine	177	1.5018	147	0.9220
6,methyl-3,ethyl-pyridine	175		164	
4,methyl-2,ethyl-pyridine	171	1.4980	122	(156)

The above figures were taken from various authors, but it must be kept in mind that different authorities give very divergent values for these constants, even differing by as much as five or six degrees in the case of the uncommon derivatives.

The above results suggest the presence of γ-collidine or 2,4,6, trimethyl pyridine; this assumption was proved by the oxidation of the substance to trimesitic acid, the presence of which was definitely confirmed. This substance has already been isolated from Fushun shale

oil by T. Eguchi (52) and from lignite tar by Krey (93). The second substance which may be present, but which is doubtful, could possibly correspond with 4-methyl-2-ethyl-pyridine. However, it was impossible to confirm its presence.

Fraction Y-3/(ii).

Corrected boiling point	198.4°
Refractive index	1.5004
M.p. picrate	not obtainable (see below)
Density	0.9390 @ 21°

The production of a crystalline picrate was made impossible by the formation of a thick dark brown tarry mass when the base was treated in accordance with the procedure given above. Every case resulted in the formation of this resinous mass, no matter how the formation of crystals was promoted, and it is interesting to note here that in 1879 - '80 Robinson made the same observation; he tried many inorganic salts (see introduction to the nitrogen compounds) but the only result was "resinous sticky masses being obtained". From later observations in the present research it seems probable that Robinson's results were due to insufficient purification. Using modern methods, Baily also found that, except in a single instance, no crystalline picrate could be obtained. However, in a later article he describes a special technique by means of which he obtained crystalline derivatives of similar bases.

Substances boiling in the range of fraction (ii) are

	b.p.	m.p. picrate	density
2,3,4-trimethyl-pyridine	192-4	163	0.9127
4-methyl-3-ethyl-pyridine	196	149	0.966
$C_{13}H_{13}N$ (Ref. No. 58)	197-9		

There is not enough available data at present in order to give any opinions as to the constitution of this fraction.

Fraction Y-3/(iii).

Corrected boiling point	206.4°
Refractive Index	1.5054 @ 20° 1.5037 @ 25°
M.p. picrate	not obtainable
Density	0.9503 @ 20°

This fraction is considered with fraction D-8/(i).

Fraction D-8.

Boiling range	213-238 with constant value at 236°
Density	0.9518
Refractive Index	1.5128
Nitrogen content	10.01%
Molecular weight	158.1
Volume percent	30.1%

When this fraction was distilled several times under the same conditions as the previous one, the first drop occurred at 203.5 and the first cut was taken between this and 206, and from there afterwards thus:-

Fraction No.	Temperature limits	Refractive index	Constant Boiling point
D-8/(i)	203-206	1.5056	206
D-8/(ii)	206-226	1.5123	217
D-8/(iii)	226-237	1.5001	227
D-8/(iv)	237-240	1.5191	239.5

This fraction, boiling between 213-238, seemed to be a transitory stage between the monocyclic and dicyclic bases. That the next fraction B-9 was of a quinoline nature was shown by sudden drop in nitrogen content and rise in molecular weight. The present fraction having an upper limit at the boiling point of quinoline does not fall in line with either the pyridine or quinoline series.

A visual analysis of the boiling points and refractive indices might indicate the presence of hydroquinolines - decahydroquinoline itself has a boiling point of 206 (Beilstein) and a refractive index of 1.4817 @ 14°, a difference of only 0.0239 from that of fraction (i). Similarly 8-methyl-decahydroquinoline has a boiling point of 208° and a refractive index of 1.4850, but both are lower than (i). As far as could be ascertained from available literature none of the ordinary alkyl substituted pyridines have a B.P. approaching that of this fraction, i.e. 206°. Even assuming that fraction was composed of highly alkylated pyridines, the value of the refractive index would be too high for consideration, as even the propyl derivative has refractive index of 1.4934.

A similar statement could be made with regard to fractions (ii) and (iii) boiling point 206-226 and 226-237. There are no less than nine alkyl deca- and tetra-hydroquinolines having a boiling point within this range of (ii). The closest to the determined boiling point are

	b.p	n_D
7-methyl-decahydroquinoline	218	1.4791 @ 14°
2,6;dimethyl;decahydroquinoline	218	1.4744 31
2,8, " " "	216	1.4777 31
Tetrahydroquinoline	218	1.5726 10

There are other subatituted hydroquinolines having a refractive index

and a boiling point closely approaching the values given above, and, therefore, it was suspected that the major portion of these cuts was composed of some such-like compounds. If these fractions contained hydrogenated quinclines, the refractive index would surely rise as the hydrogen atoms were removed, and with this end in view, a representative sample was taken and dehydrogenated according to the method of Diels and Karstens (34):-

Five grams of the mixed bases together with 7 grms. of powdered selenium were heated in a glass vessel at 185±1.5° for 38 hours and the change in refractive index noted.

The refractive index before treatment = 1.5126 @ 21°
after = 1.5128 @ 18°

From a consideration of the hydroquinolines, it can be calculated that the removal of four hydrogen atoms would cause an increase in the refractive index by an amount varying from 0.038 - 0.032, an increase which could be easily detected by refractometric methods. This argument proves the absence of hydroquinolines in more than minute amounts.

In the light of later work, it seems probable that this fraction consists of more than one type of substance, but at the actual time, no explanation could be given. Later it is hoped to return and elucidate the above difficulty.

FRACTION B-9.

Boiling Range	238-250
Density	0.9778
Refractive Index	1.5199
Nitrogen content	9.39%
Molecular weight	169.9
Volume percent	21.0

When this fraction was fractionated several times, the following results were obtained:-

Fraction No.	Temp. Limits	Refractive index	Const. value of B.P.
i	238-240	1.5193	239.5
ii	243-245	1.5197	243.5
iii	245-248	1.5199	246.5

FRACTION B-9.

DISCUSSION.

From this fraction onwards it can be seen that there is a sudden drop in the nitrogen content while the refractive indices and molecular weights still rise. The percentage of nitrogen in trimethyl-quinoline is 8.2% and the molecular weight is 171.1, the nitrogen content of the dimethyl and monomethyl derivatives is 8.9 and 9.8 respectively. Therefore, one is lead to believe, by the above information, and also by that derived from other sources, that there are, in the upper fractions di- or tri-methyl quinolines. There are, however, two important properties which have not yet been explained - the low values of the refractive index and of the density.

From the preliminary work, the presence of the quinolines is indicated, but members of this series boiling between 240 and 290° (mono-, di-, and tri-methyl quinolines and similar compounds) have refractive indices varying from 1.5828 to 1.6154. It was shown by treatment with selenium as before that the low values of refractive index for fractions B,O, and A are not due to the presence of hydrogenerated tertiary aromatic amines. A representative fraction was treated with selenium at an elevated temperature for 29 hours, after which the value of the refractive index was measured.

Value before treatment	1.5265	@ 20°
after	1.5267	@ 18°

Now it can be seen that these fractions have probably, for their major portion, the trialkyl-quinolines. After trying several experiments, the writer came to the conclusion that there was, in conjunction with the tertiary bases, another substance, or series of substances, which possessed low indices and densities. In the light of the recent work in America, under Baily, some success was expected by using the method described in his articles, and indeed this procedure of 'cumulative extraction' was a pronounced success when tried with Tasmanite shale oil bases.

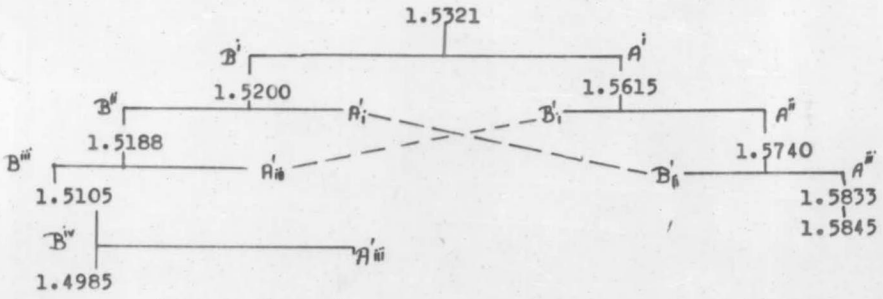
Cumulative extraction of the bases boiling over 238°C.

The work of Baily (58) and his collaborators has shown that there is in the nitrogen-containing bases of Californian petroleum another type of substance present, as well as the tertiary aromatic amines. This second type has been termed by him a 'naphthenic' base. It is apparently tricyclic and contains a piperidine nucleus and it seems probable that similar compounds may occur in the bases contained in Tasmanite shale oil.

The process of cumulative extraction was applied to the united fractions boiling between 240° and 290° of Lot 11. The refractive

index was 1.5321. They were dissolved in 1:1 hydrochloric acid and treated with chloroform according to the process of Baily (58), the aqueous layer containing the aromatic quinoline-like bases was washed with decreasing volumes of chloroform, and the chloroform layer washed with gradually decreasing volumes of water, and at each stage the refractive index was taken - this enabled one to exercise control over the effectiveness of the extractions.

The scheme is shown below in the form of a flow-sheet. As this investigation was not, at present, concerned with the structure of the chloroform-soluble bases , only the ultimate values of each measurement are shown.



It can be seen that we are dealing with exactly the same set of conditions experienced by Baily, and we are now in a better position to explain some of the previously inexplicable results found in the earlier part of the work, e.g. the non-crystalline picrates and the low values of the refractive index and density. The values of the refractive index and density in A (iii) being now definitely within the range of the trimethyl quinolines.

The purified aromatic bases were a sticky semi-crystalline mass of a light yellow colour and possessing a slight greenish-yellow fluorescence. Their odour was the characteristic one associated with the bases of this oil. Refractive index was 1.5833 @ 22° and density about equal to one. (see later).

The chloroform washings of the 'B' side were put aside, but before doing so, the chloroform was removed by evaporation and the bases freed by treatment with caustic soda. The properties of the isolated bases can be ennumerated as follows:-

(1) Colour - brownish-red.
(2) They gave the 'pyrrol' reaction with a pine shaving moistened with hydrochloric acid, a most interesting result

These fractions were more or less solid masses, but they resisted all attempts to obtain them in crystalline form.

Attempts were made to prepare crystalline derivatives but still without success. The picrates were definitely solid masses but were amorphous smears and when heated, they became converted into orange, tarry masses. This positive refusal to form crystalline picrates can be explained thus:- There occurs in the same boiling range, more than one structurally akin substance, e.g. 2,3-dimethyl-quinoline and 2,3,8-trimethyl-quinoline, both boil at 273°. Some authorities give 267° as the b.p. of 2,3-dimethyl quinoline.

This last distillation leads to several interesting results. The fact that is noticed at first glance is the high value of the refractive index in the 271°-273° boiling range, the inference to be drawn from this being the presence of dimethyl quinolines, together with the higher ones. An analysis of available figures show:-

Compound	Boiling Point	Refractive Index
2,3,4-trimethyl-quinoline	285	
2,4,5- " "	Not obtainable	
2,3,7- " "	285	
2,6,8- " "	260	
2,3,8- " "	273 (276)	1.5828
2,4,8- " "	280 (275)	1.5855
2,3-dimethyl-quinoline	273 (261 & 265)	
2,4- " "	274 (264)	1.6090

(The boiling points enclosed in brackets are other values that have been recorded. Preference has been given to figures appearing in original articles by reliable authorities rather than to tabular information published in chemical dictionaries and handbooks.)

These results lead to the assumption that fraction (iii) contains either 2,3,8-trimethyl-quinoline, 2,4,8-trimethyl-quinoline; or both of them, whilst in fraction (ii) the dimethyl-quinolines occur. The first and last fractions do not seem to fall into the general line of facts, both having low values of refractive index; 2,3,4-trimethyl-quinoline boils near that of (iv) but the refractive index is much too low and is in the range of the hydroquinolines. As far as can be ascertained, no alkyl-substituted quinoline boils near 244.5; 2,4,8-trimethyl-decahydro-quinoline boils at 243°, the presence of which is not possible from dehydrogenation experiments. Quinaldine boils at 246, but the refractive index is much too high - 1.6091 @ 25.4°. The value of the refractive is too high for the aliphatic amines, and at present no explanation seems to be satisfactory.

(3) They formed the characteristic red 'pyrrol' precipitate with hydrochloric acid.
(4) They possessed a refractive index of 1.4985, which is much too low for the quinoline derivatives and is even in the vicinity of pyrrol itself (1.5035).

It is believed, however, that the structure of this type is very complex, and when the diversity of hydrocarbons and other types occuring in the oil is remembered, one can readily realise that research into the structure of such nitrogeneous bodies is beyond the scope of the present research. Such research, if undertaken, by one student would probably occupy several years.

To return to the final stage in the water-soluble basic hydrochlorides. These were converted into their picrates, in solution buffered with sodium acetate, purified and heated with ammonia, from which the bases separated out as nearly solid resinous masses. The mixed bases were placed in distilled water and the water gently heated. When the water was cold, the general mass floated, but on warming the mass liquified and sank to the bottom of the test tube. Thus it can be seen that the bases had a density practically identical to that of water at 40°, i.e. 0.9942; on dehydration they had a refractive index of 1.5845. The bases were dissolved in absolute ether and attempts to get them to crystallise were made, but without success.

Cut O & A.

'Cumulative' Extracted

Boiling Range	270-290
Density	0.9953
Refractive Index	1.5801

Cuts O and A were united and repeatedly extracted the hydrochlorides with chloroform, the chloroform washings being disregarded. The refractive index rose from 1.5280 to 1.5801 after six extractions. After the united fractions had been washed, they were converted in to their sulphates and treated with acetone. The free bases liberated and resulting sticky mass was placed in a small flask, and carefully distilled - the apparatus being described on page 85. The distillation results were:-

Fraction No.	Temperature limits	Refractive index	Constant value of B.P.	Density
i	244-245	1.5683	244.5	
ii	271-273	1.5906	273	just
iii	277-279	1.5832	279	greater than
iv	284-285	1.5748	284.5	unity

The presence of the Quinoline Ring in the Higher Bases.

A small quantity of the non-"extracted" bases were taken and boiled in a litre distilling flask containing 100 ml. of a 2% solution of potassium permanganate. A reflux condenser was attached to the top of the flask and a small air leak extended to the bottom. Through this air leak a slow steady current of air was drawn in order to agitate the precipitated manganese dioxide, but even this precaution did not entirely eliminate the bumping. As the permanganate solution was decolourised more of the permanganate solution of increasing strength was added until the solution remained a pink colour; this process took approximately 15 hours.

The precipitated manganese dioxide was filtered off and the solution made acid beyond its neutral point with 2 ml. of nitric acid. The filtrate was a very pale stone-coloured liquid. It was slowly distilled and most of the distillate put aside for further examination (iii). The nonvolatile matter in the flask was placed in a thimble and extracted in a Sohxlet extractor for about five hours and the material soluble in alcohol collected (i). The alcohol-insoluble residues in the thimble were soluble in water.

The oxidation product was thus separated into:-

(i) The alcohol solubles.
(ii) The water solubles.
(iii) The volatile constituents.

(i) The Alcohol Solubles.

The yellow alcoholic solution was slowly evaporated in a steam bath and the residue was a sticky honey-like mass. Several methods were tried to determine its structure, but they were unsuccessful, and finally it had to be abandoned. Results tended to show that it was probably a portion of the non-quinolinic part of the bases, which according to other investigators are very stable, both to alkaline or neutral potassium permanganate oxidation. These 'naphthenic' bases are soluble in alcohol.

(ii) The Water Solubles.

The alcohol insolubles were dissolved in water, and silver nitrate was added; this caused an immediate precipitate of a dirty white colour, which was filtered off and dried. The filtrate had a distinct greenish-yellow fluorescence. Portion of the sample was weighed, ignited and dried to a constant weight. The percentage of silver amounted to 65.3%. The silver salt was purified and the free acid was obtained by the action of hydrogen sulphide on it. No attempt was made to crystallise, owing to the difficulties encountered by Hantzsch (60). The reaction with ferrous

sulphate indicated a carboxylic group in the α-position. When converted to its barium salt and dry distilled, the odour of pyridine was definitely observed. The same smell arose when the acid was distilled with slaked lime.

The Volatile organic acids (ii).

The dirty yellowish-white liquid, resulting from the distillation of the oxidation products, was treated with sodium carbonate according to the ordinary laboratory procedure; the solution was filtered and the filtrate acidified by adding nitric acid, then ammonia was added with caution until the solution was just alkaline and the solution gently boiled. Following this, dilute sulphuric acid was added until the solution had an acid reaction. The resulting liquid was extracted with ether and the etherial layer removed, the ether was allowed to evaporate off.

The residue from the above treatment was a sticky mass with a peculiar odour. It was heated with phosphorus trichloride till all reaction had ceased, allowed to cool. The crude acyl chloride was added very cautiously to strong ammonia solution immersed in a freezing bath and allowed to stand over night. A few crystals had collected at the bottom of the flask. The solution was gently evaporated and the residue recrystallised from alcohol. These crystals had a rather unsharp melting point at 114°. The m.p. of pentanamide is 114.6°. They were dried and dissolved in excess of aqueous potassium hydroxide, and heated under reflux until the fumes ceased to have had any effect on tumeric paper, the acid was then liberated, extracted, concentrated and warmed with sulphuric acid and alcohol; a distinct fruity odour reminiscent of apples, was noticed. The anilide had a m.p. of 58°. Thus, the presence of n-valeric acid was confirmed. It is a moot point whether this acid was produced from the quinolinic portion of the bases or from some other substance or substances present.

The presence of valeric acid in the oxidation products leads to the assumption that there were fairly long side chains in the 'pyridine-half' of the quinoline molecule. From the determination of other properties such as nitrogen content and molecular weight, this is impossible. There was no evidence indicating that simplier aliphatic acids were present. All of these results prove that the side chains contained only one, or possibly two, carbon atoms.

From other considerations, the presence of valeric acid can only be explained by assuming that it arose, not from the oxidation of the true aromatic bases, but from some other type of compound.

Thus it has been shown that the aromatic nitrogenous bases, ~~which~~, on oxidation, lead to the production of pyridine carboxylic acids, which from the percentage of silver in the silver salt and basicity measurements, gives a molecular weight of 233.6 for the acid. This is about half way between pyridine tricarboxylic acid (211.1) and pyridine tetracarboxylic acid (255.2) but is fairly close to methyl-pyridine-tricarboxylic acid (226.08). Two of these carboxyl groups can be accounted for by the disintregation of the quinoline nucleus, so there are two side chains in the 'pyridine half' of the molecule, one of which is apparently a methyl radicle. Whether a dimethyl-pyridine-tricarboxylic acid is formed from the potassium permanganate oxidation of any quinoline derivative is not known, no literature could be found dealing with pot.permanganate oxidation of alkyl-quinolines.

From a study of the molecular weights of the base and acids, it can be seen that we are dealing either with an ethyl-methyl, or a trimethyl quinoline, and later it will be shown that the former is not possible. That the major portion of the bases boiling around 280° are trimethyl-quinolines has been shown; there is one methyl group in the 'benzene half' of the molecule and two similar ones attached to the 'pyridine half' of the molecule.

When the acid was heated and then coupled with resorcinol, a deep red substance was formed which had a red to dirty-yellow colour change from acid to alkaline solution; if phthalein formation has occurred, there must have been the previous formation of an anhydride, necessitating two carboxyl groups in the ortho position to one another. Further proof of this orientation lies in the fact that it was found by using formaldehyde that two and not three hydrogen atoms were replaced by carbinol. According to the results of Königs (61) this will only occur when the ortho position to the methyl radicle is substituted, that is, as long as the benzene ring is not acting as the ortho substituent.

Phthalone formation requires a methyl or methylene group in the α or γ-position. A small amount of base was heated for five hours at 165° with an equal weight of phthalic anhydride and half its weight of zinc chloride, the resulting compound was a fine deep-red solid which dissolved in boiling alcohol to give crimson-orange solution.

The absence of the formation of quarternary ammonium salts by methyl iodide may well be explained by reference to the results of Decker (67). He found that ortho or ana substituted quinolines exhibit steric hinderance in that they do not form quarternary ammonium compounds with alkyl iodides.

Oxidation with chromic acid gave brownish needles, soluble in hot water. On heating they blackened about 254°. The distillation of the barium salt gave a drop or so of liquid with refractive index 1.6053. Oxidation with potassium permanganate with subsequent heating of the crystalline acid, followed by distillation with lime, gave quinoline itself.

Summary of the portion boiling above 250°.

The compounds boiling over and about 250°, consist in the main part of tertiary bases of the quinoline series, but results show that a second type of basic substance occurs, which possesses a low refractive index, and , probably contains in some part of its structure a pyrrol nucleus.

The aromatic bases present had densities and refractive indices characteristic of the quinoline homologues.

The presence of hydroquinolines was improbable from a study of the refractive indices before and after dehydrogenation with selenium.

It can be seen that alkylated quinolines are present and on oxidation with potassium permanganate, the pyridine carboxylic acids thus formed were in accord with this hypothesis.

The side chains attached to the nucleus were methyl radicles (with perhaps ethyls in much smaller amounts in the lower bases). There were two methyl radicles in the 'pyridine half' of the molecule, one of which was in the α-position, the other most probably in the β-position. With regard to the other radicle, this was in the 5: or 8: position as shown by steric hindrance.

When one remembers that it is impossible to separate certain bases by however complex and elaborate a fractionation, it can be seen that, even if the non-quinoline compounds were absent, the problem is by no means an easy one, and even now some points have arisen which still remain to be cleared up, for example, the position of the methyl group in the 'benzene half' of the molecule. There is also the structure of the non-quinolinic portion of the bases, but this would be, probably, a complete line of research in itself.

COMMERCIAL USES AND TOXIDITY OF SOME NITROGEN COMPOUNDS.

The use of pyridinic compounds in the denaturing of alcohol is quite wide spread and is coming more into the foreground lately on account of the poisonous nature of methyl alcohol. Some of the pyridine homologues are being used as solvents, but as it has already been shown - see previous pages - the greater part of the basic nitrogen compounds occurring in Tasmanite shale oil are of quinolinic nature. These basic compounds have been suggested as insecticides (C.A. 22/4789. U.S.P.1,686,136) also lubricating oils are said to have been improved by the addition of about 1% of base to them. These basic bodies are said to have an inhibiting action in pickling solutions, and also have been suggested as anti-knock agents.

Dyes. The familiar quinoline yellow-S (the sulphonic acid of the phthalein formed by the condensation of 2-methyl-quinoline and phthalic anhydride) is a valuable dye for wool and silks, other dyes of similar constitution exist. Dyes of a different type are the cyanines (and iso-cynanines). These are not applicable as textile dyes on account of their fading when exposed to the action of light, but are used extensively as photo-sensitizing agents in infra-red photography.

Fungicides. W. H. Axe and co-workers (62) have found that cultures of Eberthella typhi are completely inhibited by the nitrogen bases of petroleum in dilution 1:600, and in even less strength (1:8400) they inhibited the growth of Staphylococcus aureus. Whilst the solutions of the bases in dilute hydrochloric acid were highly bactericidal, the bases emulsified with soap were not so.

Toxicity. Some of the lower alkyl quinolines are found to arrest the development of plants and Ciamician and Ravenna (55) report specifically that 2-methyl-quinoline is highly toxic to plant life.

The present writer found that the vapours of the Tasmanite shale oil bases produced grave effects on the general constitution, such as acute headache, sick feeling. An inflamed throat resulted from working with bases and their vapours for even only six to ten hours. Dyson reports (54) that decahydroquinoline paralyses the motor nerve endings while tetrahydroquinoline acts as a heart poison and gives rise to sweating and shivering.

As a substitute for quinine, the hydroxy derivative of kairoline has been suggested and kairoline can be synthesised from tetrahydroquinoline and methyl iodide. These hydrogenated products can be prepared from such basic compounds. Also such widely used antiseptics as pro- and acri-flavine are amino derivatives of acridine, the tricyclic nitrogen-containing compound corresponding to anthracene and it is quite likely that investigation on the

PART IV. THE SULPHUR COMPOUNDS.

Sulphur is always present in shale oil, and according to Perkin (68) if, either a shale oil or petroleum contains sulphur at all, then each and every fraction, no matter how closely cut, will show the presence of sulphur compounds. A similarity exists between the sulphur compounds which occur in petroleum and those in shale oil, but, broadly speaking, we find that aromatic sulphur compounds seem to predominate in shale oils and in the case of petroleum - aliphatic sulphur compounds have first place. This statement can be applied in a general way to the hydrocarbons also.

The examination of the sulphur compounds present in shale oil presents a more difficult problem than the corresponding one in petroleum, on account of the much greater unsaturation of the former. On an allied subject 'The Examination of Low Temperature Coal Tars' Morgan and Soule (69) state - "There is no concentration of sulphuric acid capable of removing such sulphur compounds without attacking the unsaturated hydrocarbons, which preponderate in the neutral oil. These unsaturated compounds interfere, moreover, with the usual qualitative thiophene identifications, by reacting with the sulphuric acid of the indophenin test and the nitric acid of the thalline test to give reddish brown shades, which mask the colour reactions even in the presence of added thiophene". This was also the case in the present investigation.

The sulphur compounds in oils have been an ever recurring thorn in the side of the technologist. They are particularly objectionable on account of the odour of the oils containing even small quantities of them, and secondly, on account of the corrosive effect of the by-products of combustion in the interior of the cylinders of the engine; these by-products are mainly sulphur dioxide with subsequent formation of sulphuric acid. Recently, Kruber and Schade (70) have shown that mercaptans and such substances possess a catalytic action for gum formation.

Probably the most extensive work on the sulphur compounds occurring in shale oil has been done by Challenger in England and by Scheibler in Germany. Challenger (71) reports that thiophenes are the chief sulphur compounds occurring in shale oil, and when the percentage of sulphur is found in the different fractions, maxima will occur at the boiling points of the thiophene homologues (see also Kurth (5)). From that portion of Kimmeridge shale oil volatile in steam, Challenger removed amines, phenols, and ketones, and then fractionated the purified oil into the following cuts (i) 75° - 93°; (ii) 109°-117°; (iii) 117°-126°; (iv) 134°-138° (v) 158° -167°, and succeeded in identifying the methyl, ethyl, and dimethyl derivatives of thiophene.

Scheibler (72) working on shale oil from the south of France, showed that homologues of thiophene were present, and later this author in conjunction with Rettig (73) proved the presence of 2-n-butyl-thiophene and two propyl thiophenes. Similar compounds have been found in Russian shale oil by Dodonov and Sochestwenskaja (74) and in Rumanian petroleum by Edeleanu and Filiti (75).

Mercaptans:- Birch and Norris (76) have identified iso-propyl and iso-butyl-mercaptan in shale oil, while Fukio Horie (77) working on the Fushun deposits, found similar mercaptans together with higher ones, such as n-amyl-mercaptan, sec-hexyl-mercaptan as well as other sulphur derivatives.

Other Sulphur containing substances in shale oil are:-

Free Sulphur	- No specific references available.
Hydrogen Sulphide	- " " " "
Carbon Disulphide	- (78).

Challenger (89) found tetrahydrothiophene in Kimmeridge oil by adding sodium chloride to the liquor remaining after the removal of thiophenes by the mercuric acetate treatment. Similar members of this series have been found in Canadian petroleum by Mabery and Quayle (80).

EXPERIMENTAL WORK.

Hydrogen Sulphide.

Hydrogen sulphide was not present in the oil; the method of Faragher Morrell and Monroe (22) and that of Wendt and Diggs (23) both gave negative results.

Elemental Sulphur. Using an inverted "Halphen cotton-seed" oil test [illegible] and (82), the absence of elemental sulphur was established. No reports that free sulphur has been found in shale oil could be located; Tervet has, however, detected this element in shale naphtha (81).

Mercaptans. The presence of mercaptans was indicated, both by the smell of the different fractions and their chemical reactions. After trying several methods for the estimation of these sulphur compounds in the fractions, the method of Bond (83) was used; this method gave good duplicate results and agreed well with more accurate methods, which were, however, more tedious and took a much longer time to perform. The results of the titrations are tabulated below (see Graph No.7). The volume of the oil sampled was 5 ml., and the cupric oleate was dissolved in cyclohexane and not in oxygen-free kerosene as advised by Bond.

Table No. 23

Fraction No.	Volume of Cupric Oleate	Percent Mercaptan sulphur	Nature of the Precipitate
A	0.05	0.0002	None
B	0.7	0.0294	None
C	1.1	0.0445	Brown gelatinous
D	1.8	0.074	Yellow gelatinous
E	2.6	0.105	White
F	2.1	0.082	White gelatinous
G	2.7	0.105	White gelatinous
H	3.7	0.126	Yellow gelatinous
I	4.3	0.164	Brown flocculent
J	6.2	0.232	Reddish "
K	7.6	0.273	Brown precipitate
L	7.8	0.282	None liquid brown
M	6.3	0.226	None Olive
N	11.1	0.390	None olive-green
O	14.7	0.507	" "
P	6.7	0.224	ditto
Q	11.5	0.392	ditto
R	12.7	0.421	
S	13.5	0.438	
T	16.0	0.515	
U	11.0	0.344	
V	14.5	0.445	

From the graph it can be seen that there are sharp peaks corresponding to the boiling points of the simple aliphatic mercaptans and minima at intermediate points. One can surmise from the results that the members of the simpler mercaptans occur. As the lower members of these sulphur compounds can be removed by an alkali wash, and most of the higher ones by suitable treatment, further work on these compounds was largely abandoned, there being present other sulphur compounds of greater interest. Efforts to isolate the mercaptans in bulk were mainly unsuccessful and any further time spent on this section of the work was not thought justifiable. Therefore, research was commenced on the Thiophenes.

THIOPHENES

Preliminary Investigation.

One litre of the crude oil was sulphonated with concentrated sulphuric acid and the resulting sulphonic acids were diluted with water, a deep yellowish oil separated out, containing much sulphur. The water soluble sulphonic acids were treated with barium carbonate until all the free sulphuric acid had been precipitated out as barium sulphate. The solution was filtered through a Buchner funnel, and the barium salts of the sulphonic acids crystallised by evaporation. Fractions of these flaky crystals gave the usual organic sulphur reactions. From this it was assumed that cyclic sulphur-containing compounds were present and an investigation of the thiophenes present in the oil was commenced.

The first stages of the investigation were performed on the Tasmanite shale gasoline and not on the 'crude' oil; the unsaturated nature of the latter making such an investigation extremely difficult indeed. Treatment with sulphuric acid to remove unsaturates may change the nature of the contained sulphur compounds. Heusler (84) makes the assertion that sulphuric acid may alter the composition of the sulphur compound even though it does not remove it, and also that an organic sulphur compound may be formed from the sulphuric acid and the olefines contained in the oil itself. Here again attention is drawn to a fact mentioned in an earlier section, namely, that during distillation new and different compounds may be formed in situ; this applies to an even greater extent to the sulphur compounds. Distillation at reduced pressures will usually result in a lower percentage of sulphur per fraction, and at low pressures the sulphur content in a given fraction may be as much as one tenth of its value if the oil had been distilled at atmospheric pressure.

SULPHONATION OF THE TASMANITE SHALE GASOLINE.

One litre of Tasmanite shale gasoline was sulphonated with fuming sulphuric acid until the acid was no longer discolored. The excess acid was neutralised with calcium hydroxide and the calcium sulphate filtered off. The aromatic calcium sulphonates were then crystallised from water solution and converted into their sodium salts and re-crystallised. When purified, the crystals were glistening white plates of distinct aromatic nature, soluble in water and alcohol, but insoluble in other organic solvents. The supposed aromatic and thiophene sulphonic acid salts were fused with caustic soda and the mass extracted with ether. Not all of the sulphonic acids were converted to phenols, but both the ether solubles and the residues reacted positively to organic sulphur.

Distillation of the Shale Gasoline.

Five litres of the gasoline were washed with dilute hydrochloric acid, then caustic soda and then fractionated in a Pyrex flask with Quickfit and Quartz fractionating column and associated apparatus. The fractionation was carried out twice with the following results.

Table No. 24

Fraction No.	Temperature Limits	Volume mls.	Refractive Index @ 19°	Sulphur % III	Density @ 18°
1	0-50	9.6	1.3834	0.204	0.6934
2	50-70	87	1.3972	0.531	0.7037
3	70-90	457	1.4088	1.176	0.7484
4	90-110	491	1.4207	1.511	0.7641
5	110-130	538	1.4364	1.974	0.7884
6	130-150	593	1.4389	2.314	0.7928
7	150-160	163	1.4469	3.063	0.8049
8	160-170	161	1.4496	3.578	0.8112
9	170-180	115	1.4558	3.841	0.8225
10	180-190	91	1.4590	3.221	0.8377
11	190-200	58	1.4654	3.018	0.8400
12	Residues	65			

The sulphur determinations were carried out in a modified A.S.T.M. lamp of the writer's own design (see diagram opposite). The oil was burnt in the small lamp (A). On account of the unsaturated nature of the oil, the different samples had to be mixed with 3-5 times their weight of sulphur-free alcohol in order to prevent the sooginess of the flames. The gases from the combustion were drawn through N/20 sodium carbonate. After a certain

time had elapsed, the sodium carbonate in column 'C' was washed down into flask 'B' with distilled water, the flask removed and the excess carbonate back titrated with N/10 hydrochloric acid. The amount of oil consumed was found by the difference in weight of the lamp before and after the experiment multiplied by the ratio of the weight of the oil to the weight of oil plus alcohol.

Fraction 3 and 4 were subjected to further and more exact fractionation thus:-

Table No.15

Fraction No.	Temperature Limits	Sulphur %	Refractive Index	Density
3a	70-75	1.02	1.4003	0.7179
3b	75-80	1.18	1.4073	0.7395
3c	80-85	1.48	1.4232	0.7583
3d	85-90	1.54	1.4180	0.7667
4a	90-95	1.48	1.4205	0.7548
4b	95-100	1.49	1.4300	0.7585

From this table it can be seen that there is a maximum in sulphur content in 3d (85°-90°) and a sudden increase in refractive index in fraction 3c (80-85)°. Benzene boils at 80.4° and thiophene at 84°, thus the sudden increase in the refractive index is probably due to the presence of both of these compounds, and the maximum of sulphur is due to thiophene. (The reason for the maximum of sulphur in 3d and not 3c being probably due to some lag, or drainage error in the condensing system.

Examination of Lot I for the presence of thiophene.

The different fractions were examined by fractionation and any liquid boiling below 76° was put aside and the portion boiling between 76° -92° was collected; this constituted Lot I.

The fraction was treated with mercuric chloride in the following manner (85):- Alcohol was added until the solution contained 80% of alcohol, and twice the amount of mercuric chloride (M/4) was then added as required to form the α-mercurichloride (assuming that all the sulphur present was thiophenic) and finally, five times the quantity of sodium acetate necessary to combine with the liberated hydrochloric acid was added to the mixture. The mixture was allowed to stand for two days, with frequent shaking. At the end of this period there was an upper layer of unattacked oil and below this the aqueous layer. On the bottom of the vessel was 41 ml. of a heavy yellow oil, density 1.3427 and below this again the precipitated mercury compounds. The heavy oil on distillation with hydrochloric acid gave an oil with a camphor-like odour, n_D 1.4361,

and which tasted faintly of pine resin or some similar material. After standing over-night, long fine needle-like crystals were formed; it gave no indophenin reaction.

Analysis of precipitate from fraction boiling 76°-92°.

The precipitate was extracted with alcohol for some time, and the purified alcohol-solubles were pale yellow in colour, and on purification and analysis gave the following figures:-

	found	calculated for $C_4H_3S.HgCl$
Chlorine	11.8	11.1
Sulphur	9.7	10.0

The melting point was rather indefinite at 177°-184° it commenced to blacken. The melting point of thiophene-mercurichloride is given at 183°.

On distillation with 6N hydrochloric acid, only a very small volume of oil could be obtained, but as there are no isomerides possible and the oil reacted positively to the usual thiophene colour tests, therefore there can be little doubt that thiophene was present in this fraction.

The Methyl-Thiophenes (113°-114°).

The 2-methyl-thiophene is of quite common occurrence in shale oils, the researches of Challenger and his co-workers (71) having proved the presence of this thiophene homologue in Kimmeridge shale oil, as well as thiophene itself.

Fraction '5' was considered as containing either, or both, of the methyl-thiophenes.

α-methyl-thiophene — Boiling point = 113°
mp. of 5-mercurichloride = 204°
Density = 1.107

β-methyl-thiophene — Boiling point = 114°
Density = 1.0247
mp. of 5-mercurichloride = 138.5

EXPERIMENTAL.

Cuts 4b and 5 were united and fractionated three times and the fraction coming over between the limits 109°-117° collected

Table No. 26

Fraction No.	Temperature Limits	Sulphur % II	Refractive Index	Density
mf(i)	106-109	2.429	1.4346	0.7642
mf(ii)	109-117	2.983	1.4345	0.7759
mf(iii)	117-126	2.996	1.4348	0.7808

The fraction boiling between 109° and 117° was fractionated twice and the final temperature limits were taken at 110° -117°; this fraction had a volume of 167 ml. and contained 2,987% sulphur. Sixty ml. of this fraction were dissolved in 1500 ml. of alcohol and agitated with one litre of 33% aqueous solution of sodium acetate and four litres of a saturated solution of mercuric chloride in water (86). After two and a half hours a dirty yellow precipitate formed, this was filtered off and the filtrate allowed to stand with frequent shaking for a further period of nearly one day, a further precipitate was then found to have been formed but of much lighter colour than the first, while a third crop nearly white in colour was obtained at the end of two days. The residual oil now contained 1,67% sulphur.

The combined precipitates were extracted with boiling alcohol, the alcoholic extract was light yellow in colour and gave, on evaporation, a cream coloured crystalline mass. The residue in the extraction thimble was a dirty, creamy, lumpy mass.

A small sample of the crystalline compound was heated in a Soya-bean oil bath in a melting-point tube; at 190° it commenced to blacken and no mp. could be obtained. On the other hand when the m.p. tube was quickly immersed into the oil at 205°, the mercury compound melted and quickly charred and on immersion into the oil at 200° it commenced to char without previous melting. On further experimenting the limits were reduced to 202° -204°. Steinkopf states that the melting point of 2-methyl-thiophene-5-mercurichloride is 204 with previous sintering. The corresponding mp. of the 3-methyl compound is given at 138°. The mercurichloride was distilled with 6N hydrochloric acid, the oily matter coming over with the water was extracted with ether and directly brominated, the bromine water was quickly decolourised and on further addition of bromine water, the tribromo product was obtained. There was difficulty in getting this to crystallise but finally, with recrystallisation from alcohol, the tribromo compound was obtained with a mp. of 84°. Further recrystallisation gave no rise in mp. The mp. of tribromo-2-methyl-thiophene is 86° (other authors give 94° and Challenger gives 87°) whilst that of the 3-methyl compound is only 35°. Gatterman etc.(87) state that a mixture of the tribromo compound of the 2- and 3-methyl isomers can not be separated by crystallisation and that it melts at 74°. Thus it appears that the 2-methyl-thiophene is the only thiophene occuring in the 109°-117° boiling range. In order to finalise the identification, a small amount of the purified distillate from the mercuric chloride treatment was oxidised with dilute aqueous potassium permanganate, the resulting solution was extracted with ether, and the etherial solution allowed to evaporate at room temperature. A small amount of white powdery crystals were obtained with a mp. of 124-125°.

mp. of thiophene-2-carboxylic acid = 126.5°
(α-thiophenic acid)
mp. of thiophene-3-carboxylic acid = 136°
(β-thiophenic acid)

The Di-Methyl and Ethyl-Thiophenes.

Dimethyl-thiophenes have been found in most shale oils; Challenger (71) isolated 3-ethyl-thiophene and 2,3-dimethyl-thiophene in the fraction boiling between 134°-138° in Kimmeridge shale oil. McKittrick (85) working on 'cracked Midway crude' found these and also 3,ethyl and 3,4-dimethyl-thiophenes. Dodanov and Sochestwenskaja (74) succeeded in detecting 2,3-dimethyl-thiophene in Russian shale oil.

Examination of Fraction 6 for Di-Methyl-Thiophenes.

Boiling Range	130°-150°
Sulphur	2.31%
Density	0.7928
Refractive Index	1.4389

This fraction was distilled several times and finally fractionated into two lots -

(6a) 130°-135° density 0.7854 @ 18
refractive index = 1.4390
sulphur = 2.189

(6b) 135°-143° density = 0.8012 @ 18
refractive index = 1.4468
sulphur = 2.940

Fraction (6a) was treated with mercuric chloride and sodium acetate according to Steinkopf and the small amount of precipitate was distilled with 1:2 hydrochloric acid. Only the slightest amount of oil came over; this was extracted with ether, and the ether allowed to evaporate off, the residue consisted of a minute quantity of white crystals - these did not give any thiophene reactions.

Sixty ml. of (6b) were agitated with 140 grm. of mercuric acetate dissolved in 800 ml. of water in a separatory funnel. Within about a half-hour, a large amount of a pure white granular precipitate was formed, while the aqueous liquor became quite yellow. The mixture was allowed to stand for thirty hours with frequent shaking and after this period the precipitate (97 grms.) was filtered off. An examination of the filtrate showed that there was no oil remaining after the mercuric acetate treatment, in other words, the whole fraction (6b) had been converted into this complex mercury compound.

The precipitate, when removed from the Buchner funnel, was of the constituency of white cream cheese; this precipitate was washed with light petroleum ether and then distilled with 1:2 hydrochloric acid, whereupon 57 ml. of oil collected in the receiver. This oil had a sweet aromatic odour, with no trace of any organic aliphatic sulphury smell, as was associated with the original fraction. It burnt with a very smoky aromatic flame, but not much sulphur dioxide could be detected in the combustion products. It had the following properties - (6c)

Volume	57 ml.
Density	0.8107
Refractive Index	1.4471
Sulphur	2.96%, 3.04%, 2.98%.

This only gave a very fleeting indophenin reaction and there was some doubt about it even then. Forty mls. were distilled in a fifty ml. Pyrex flask, the whole of the distillate came over between the limits 135-141°.

Fraction No.	Temperature Limits	Refractive Index @ 21°	Volume ml.
6c(i)	135-137	1.4469	12.4
6c(ii)	137-139	1.4470	20.0
6c(iii)	139-141	1.4467	7.5

compare the refractive index of (6c) i.e. 1.4471.

Fifteen ml. of 6c(ii) were subjected to the action of mercuric chloride as before, and gave a yellowish precipitate.

The precipitate from the action of the mercuric chloride was distilled with hydrochloric acid when about one ml. of an oil was produced, refractive index 1.4584. This ml. of oil was also water-white with a clean aromatic-thiophene odour, and burnt with a smoky flame. It decolourised very slowly a weak solution of potassium permanganate. Excess bromine water gave a reddish brown product, heavier than water, but no crystalline deposit could be obtained.

DISCUSSION.

In the case of the 2,5-dimethyl-thiophene-5-mercurichloride, there is a direct covalent linkage between the mercury atom and the carbon. These compounds are true primary valence compounds and in contrast to them are the addition compounds, which are formed from organic sulphides etc. and mercury salts, which containing only residual valencies, are split up by caustic with the formation of the oxide of the metal. There was very little of the oxide to be seen when a portion of the precipitate was

treated with aquatic acids, but there was no doubt that a little of the oxide was produced.

A study of the refractive indices will show that the index remains practically unchanged from beginning to end (1.446 - 1.447) and never rises near that of the dimethyl-thiophenes (1.5138). The density was also much too low. The boiling point limits of 135°-141° correspond fairly correctly with the dimethyl and ethyl-thiophenes and completely exclude other sulphur compounds, such as disulphides or mercaptans boiling within the range, e.g.:-

	b.p.		b.p.
n-propyl-thiether	142	methyl-disulphide	117
ethyl- thiether	90.5	ethyl- disulphide	153
pentanethiol	126	tetrahydrothiophene	119
hexanethiol	150	pentamethylene sulphide	141.4

The smell also excludes most sulphur compounds, as the thiophenes, according to Ubbery, have a very bad smell, and the smell of most aliphatic sulphur compounds needs no elaboration, whereas this oil had a very clean smell.

That the fraction was largely aromatic, or of a cyclic structure was shown by the nature of flame and of its solubility in concentrated sulphuric acid. The density is too high to contain much cyclanes, even supposing that it were possible to precipitate them with mercuric salts, and too low for the aromatics, as is also the refractive index.

The properties agree fairly well with the cyclenes, however, for example 1:1:2:3-tetramethyl -, -cyclopentene boils at 135.2

density 0.8035

refractive index 1.4441.

Such insaturates combine with mercuric salts, but this, in no way, explains the 3% of sulphur.

Forty mls. of fraction (6c) were refluxed with Dimroth's reagent (88); after one hour, a large amount of dirty stone-coloured precipitate was formed (60.6 gms) and no oil remained. This was washed with petroleum ether, steam distilled to remove any occluded hydrocarbons, and then distilled with hydrochloric acid, whereupon a light yellow oil came over. This oil was distilled over metallic sodium, the whole of the distillate boiled between 135°-142° and had a clean aromatic odour and refractive index of 1.4475. It was then sulphonated with sulphuric acid and the calcium sulphonates prepared in the usual manner.

SECTION V. THE ACIDIC CONSTITUENTS.

The Phenols

Three hundred of the acidics obtained from the crude oil by treatment with 10% caustic soda, followed by neutralisation with sulphuric acid, were distilled under reduced pressure in order to free them from any inorganic matter. The distillate was light red in colour and had the characteristic phenolic odour.

density 0.9843 @ 19°
refractive index 1.5142

175 mls. of the crude distilled phenols were taken and dissolved in 500 mls. of 4N caustic soda and the solution made up to one litre. A steady stream of carbon dioxide was passed through the caustic solution until all the phenols had been liberated, these were removed, and then the naphthenic acids were put out of solution with hydrochloric acid and placed aside for a later investigation.

The volume of the liberated phenols was 124 mls. density 0.997 refractive index 1.5274

They were distilled with the following results:-

Fraction No.	Boiling Range	Volume	Density	Refractive Index
1	183-204	2.0	0.9811	1.5346
2	204-207	12.3	1.0119	1.5330
3	207-217	13.4	1.0738	1.5321
4	217-226	24.5	1.0216	1.5287
5	226-233	31.1	1.0285	1.5253
	residues			

Fractions 1 and 2.

Fraction 1 gave the following colourimetric reactions:-
(i) greenish colour with ferric chloride
(ii) bright red on warming with chloroform and caustic potash

The united fractions 1 and 2 were refractionated three times and divided into the following cuts -

Cut No.	Boiling Limits	Constant B.P.	Density	Refractive Index
i	200-203	203.6	1.021	1.5201
ii	203-208	207.4	1.018	1.5220
iii	208-214	211	1.011	1.5284

With regard to the portion coming over before 200° - from the colour reactions it appeared that only a minute amount of phenol, if any, was present.

All the fractions were water white with the characteristic cresol odour and a very faint sulphury smell - all thiocresols boil below 200°.

Fraction 2/1

Boiling Limits	200-203
Constant boiling point	202.6 @ 754 mm.
Density	1.021 @ 18°
Refractive Index	1.5201
Volume	8.1 ml.

This fraction was washed with dilute sodium carbonate solution followed by a mercuric chloride treatment to remove traces of sulphur compounds, washed with water and the water extracted with ether, the water insolubles and the etherial extract were united and then dried.

This cresol extract was again distilled, which caused the major portion to boil between 202±0.4. A boiling point determination gave 202.6 @ 749 mm. density 1.027 and n_D 1.5278, both at 19°. All attempts to cause solidification (down to -15°c) were unsuccessful, as were attempts to obtain the bromo product. Ferric chloride gave a greenish-blue shade. Distillation with zinc dust yielded toluene.

Schotten-Baumann Reaction:- 0.75 grm. was taken and 5 ml. of water added, then 1.3 ml. of benzoyl chloride and the solution made alkaline with 10% caustic soda, shaken and gently warmed, allowed to stand and then poured into water. The water was extracted with ether and the etherial solution allowed to evaporate; the residue consisted of white flakey crystals with a smell like benzoic acid but more acrid. These crystals had a m.p. of 50.7° which rose to 53.1° after recrystallisation and further purification

m.p. of m-tolyl benzoate	54°	(90)
	56°	(91)

Another portion was nitrated according to the method of Bassie (92) extracted with ether and recrystalised from water. The product had a m.p. of 104°, m.p. of 2,4,6,trinitro-m-cresol = 106°. According to Berzens (91), anhydrous sodium acetate forms with m-cresol a complex $5 \cdot AcONa, 2 \cdot MeC_6H_4OH$, soluble in the usual organic solvents, which on decomposition with water yields m-cresol in a high degree of purity. This reaction, so the author maintains, is specific to m-cresol and he published new data for this compound and asserts that previous information is erroneous on account of impurities.

d^{15}_4 = 1.039 m.p 11.8 b_{760} 202.5

Similar procedure was applied to the purified m-cresol from the shale oil, only a drop or so was obtained and it had a clean cresol smell and solidified at 10.4°; the refractive index was 1.5343 at 20° which is practically the same as given by Darzens (1.5352) and agreed more closely than the laboratory m-cresol (B.D.H.) which did not solidify even at a temperature of -17 and had refractive index 1.5446. Attempts to detect the ortho- and para-compounds were not very successful and up to the present their occurrence has not been confirmed.

Further research on the phenols present in Tasmanite shale oil is in progress.

PART VI. SUMMARY and CONCLUSIONS.

For the purposes of clarity, the research is not summed up as a whole but under the different sections into which the work is divided.

Part I:- A general outline is given of the shale position in Tasmania as regards the occurrence, history and geology. The oil-producing substance of the shale consists of small discs of vegetative origin and are very similar to Lycopodiaceous macrospores. During the retorting of the shale, there are primary and secondary pyro-bituminous decompositions in which the kerogen breaks down into an unsaturated oil, and then this intermediate product decomposes to yield the shale oil.

Part II:- From the laboratory results it appears that Tasmanite shale oil is an unsaturated oil with a relatively high aromatic content. The oil was distilled and cuts were taken at ten degree intervals in the lower fractions and at twenty degree intervals in the higher fractions.

The resulting fractions were washed with suitable reagents in order to estimate the amounts of acidic and basic compounds present. The maximum amount of acidics present was nearly six percent, and the corresponding figure for the basic material was 4.5%. The degree of unsaturation was estimated by solubility in 85% sulphuric acid and varied between forty and forty-seven percent, while the aromatic content was up to one quarter of the oil - by volume. The presence of di-olefines was established, and, in comparison with other oils this oil is very rich in this type of hydrocarbon. The high unsaturation and di-olefine content makes this oil unsuitable for fuel purposes, but it might be possible to utilise the unsaturates in other ways, for instance, in some manufacturing processes for plastics. di-olefines are one of the primary constituents. It is probable that terpenes, or substances closely allied to them, occur in the oil, but their presence was not confirmed.

Part III:- A short account of the nature of the basic nitrogenous compounds that occur in other shale oils is given, and in general, similar compounds were found in Tasmanite shale oil. The major portion of the bases was of a quinolinic nature, but other highly complex nitrogen-containing bodies were also present; the latter, on reduction gave an unexpected and interesting result, in that a compound of apparent alkaloidal nature was produced.

The tertiary aromatic bases consisted of alkylated quinolines and trimethyl-pyridine. Their constitution was proved by oxidation to carboxylic acids and by other reactions. The fractions boiling near 270°C possessed three methyl groups attached to the quinoline nucleus and their orientation was found (see page 49). Possible use of substances similar to the above were discussed.

Part IV:- Tasmanite shale oils contain large percentages of sulphur which reaches 3.5% in the 160°-170° boiling range. The cyclic sulphur-containing substances were of thiophenic nature and the following thiophenes were identified:- thiophene, 3-methyl-thiophene. Owing to difficulties outside the research no higher derivatives have been identified as yet. No hydrogen sulphide or free sulphur were detected and the nature of the mercaptans and other acyclic sulphur compounds was not investigated.

Part V:- Work is in progress investigating the nature of the phenols that are contained in the oil. Phenol itself was not present to any extent and the lowest members identified were cresols. m-Cresol was prepared in a high degree of purity and its characteristics found.

Part VI:- A short summary of the contents of the thesis is given.

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